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SIMULTANEOUS FLOW OF HEAT AND WATER IN  
PLANT TISSUE

by

Gaylon Sanford Campbell

A thesis submitted in partial fulfillment  
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Physics

UTAH STATE UNIVERSITY  
Logan, Utah

1966

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Gaylon S. Campbell

# TABLE OF CONTENTS

INTRODUCTION . . . . .	1
REVIEW OF LITERATURE . . . . .	3
Early observations . . . . .	3
Recent experimental work on thermo-osmosis across membranes . . . . .	3
Recent experimental work on thermo-osmosis in soils and other porous bodies . . . . .	4
Application of irreversible thermodynamics to biological systems . . . . .	5
The application of irreversible thermodynamics to thermo-osmosis . . . . .	6
Type of system necessary for non-zero values of $Q^*$ . . . . .	14
Membrane models and their relationship to $Q^*$ values . . . . .	18
Conclusions from the literature review . . . . .	24
EXPERIMENTAL METHODS . . . . .	25
Preliminary studies . . . . .	25
Experimental determinations of the apparent heat of transfer . . . . .	34
Determination of $Q^*$ from thermo-osmotic pressure difference and thermo-osmotic flow . . . . .	40
Other experiments on thermo-osmotic pressure difference . . . . .	62
DISCUSSION AND CONCLUSIONS . . . . .	64
General . . . . .	64
Thermo-osmotic membranes . . . . .	65
Properties of cell membranes as indicated by thermo-osmosis experiments . . . . .	66
Size of $Q^*$ values . . . . .	67
Time and space dependence of $Q^*$ . . . . .	69
SUGGESTIONS FOR FUTURE WORK . . . . .	71
LITERATURE CITED . . . . .	73
APPENDIX . . . . .	76



# LIST OF TABLES

Table	Page
1. Apparent heat of transfer for several values of temperature (T), water potential ( $\psi$ ), and chemical potential gradient ( $\Delta\mu_w$ ) <sub>T</sub> . Values of T, $\psi$ , and ( $\Delta\mu_w$ ) <sub>T</sub> were taken from Figures 14 and 15 . . . . .	37
2. Osmotic potentials and buildup rates for solutions taken from reservoirs of thermo-osmotic pressure apparatus . . .	54
3. Coefficients of the quadratic equation of best fit for the data in the figure indicated and the time indicated. The equation is of the form $\Delta h = At^2 + Bt + C$ . . . . .	58
4. Values of $L_{ww}$ , $L_{wq}$ , and $Q^*$ calculated at 15 minute intervals using equation [9] and the data obtained from the thermo-osmotic flow experiment. The values labeled "max." were calculated from equation [10] . . . . .	60
5. Values of $L_{ww}$ , $L_{wq}$ , and $Q^*$ calculated using equation [9] and using the difference in hydraulic pressure plus the difference in osmotic pressure between the reservoirs as the driving force . . . . .	61

# LIST OF FIGURES

Figure	Page
1. Isolated system consisting of reservoirs separated by a porous partition . . . . .	7
2. Apparatus for measuring the thermo-osmotic pressure difference . . . . .	10
3. Apparatus for measurement of thermo-osmotic flow . . . . .	11
4. System for demonstrating the simultaneous flow of water and heat. System consists of two water reservoirs separated by a porous partition, D . . . . .	16
5. System of potential energy barriers encountered by water moving through a lipid membrane (adapted from Danielli, 1952) . . . . .	20
6. Diagram of a polar membrane pore (from Danielli, 1954) . . . . .	22
7. Possible system of potential energy barriers encountered by a water molecule passing through a polar pore . . . . .	23
8. Apparatus used in preliminary thermo-osmosis studies . . . . .	26
9. Temperature gradient for preliminary apparatus. The sample used is from a potato tuber . . . . .	29
10. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg solution of carbowax 400 and was subjected to the temperature gradient for 18 hours, 33 minutes . . . . .	30
11. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg solution of carbowax 400 and was subjected to the temperature gradient for 24 hours, 45 minutes . . . . .	31
12. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg carbowax 400 solution and was subjected to the temperature gradient for 24 hours, 14 minutes . . . . .	32
13. Apparatus for determining the apparent heat of transfer . . . . .	35

Figure	Page
14. Water potential distribution as a function of temperature in a 1.2 cm long, 1 cm diameter potato sample. Sample was subjected to an 8.3 centigrade degree/cm temperature gradient for about 14 hours . . . . .	38
15. Water potential distribution as a function of temperature in a 1.2 cm long, 1 cm diameter potato sample. Sample was subjected to an 8.3 centigrade degree/cm temperature gradient for about 14 hours . . . . .	39
16. Apparatus for measuring thermo-osmotic pressure difference . . . . .	42
17. Pressure difference vs. time for a section of potato tuber which is subjected to a temperature gradient of 6.25 centigrade degrees/cm. Positive values of $\Delta h$ indicate the pressure is highest on the cold side . . . . .	43
18. Pressure difference vs. time for a section of potato tuber which is subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ indicate the pressure is highest on the cold side . . . . .	44
19. Pressure difference vs. time for a section of potato tuber which was subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ indicate the pressure is highest on the cold side . . . . .	45
20. Pressure difference vs. time for a section of potato tuber which was subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ are for highest pressures on the cold side . . . . .	46
21. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ indicate pressure buildup is on cold side . . . . .	47
22. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ indicate pressure is highest on cold side. After 1 hour, 45 minutes, no more readings were possible because the water had reached the top of the cold side manometer tube . . . . .	48
23. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of $\Delta h$ indicate a pressure buildup on the cold side. The initial dip was probably due to thermal expansion and contraction of the water and tissue . . . . .	49

24. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a pressure buildup on the cold side . . . . . 50
25. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a pressure buildup on the cold side. The small pressure buildup on the cold side followed by the flow toward the hot side apparently indicated a more rapid movement of osmotically active materials into the water of the hot reservoir than occurred on other replications . . . . . 51
26. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a buildup of pressure on the cold side. The sample used for this replication was placed in the apparatus for about three hours and then taken out and washed and replaced in the apparatus. This apparently prevented the buildup of osmotically active substances in the hot reservoir. The tissue is, however, much less permeable to water than were samples in other replications, probably due to the lack of aeration . . . 52
27. Graph showing the decrease of osmotic potential of water which covers a sample of potato tuber tissue . . 56
28. Graph showing a titration of the solution from one of the reservoirs of the thermo-osmotic pressure difference apparatus. The solution was diluted to 1 part in 10, and titrated with  $\text{Na}_2\text{CO}_3$ . Two possible inflection points are shown by arrows . . . . . 57
29. Probe and sample holder for measuring freezing point depression . . . . . 78
30. Circuit used to measure freezing point depression . . . . 79

## INTRODUCTION

Although biological phenomena may be partially described in a general way without the use of mathematics and physics, the experimental results may be more meaningful if they are analyzed on the basis of physical and mathematical laws. The complexity of biological systems has made the application to them of mathematics and physics rather difficult, and only recently has much progress been made. Although it has yet been possible to describe only a few simple biological systems by actual equations, a great deal of qualitative information may be obtained by applying physics and mathematics. Russell (1960, p. 439) said

In principle at least, the properties and processes of living plants may be described by the terminology and laws of physics. Such properties as color, mass, volume, area, viscosity, elasticity, specific heat, and permeability; and such processes as diffusion, reflection, osmosis, heat conduction, fluid flow, absorption, and swelling are examples of physical concepts useful in describing living plants.

He also states that

The reactions encountered in biological systems are in the main highly irreversible; therefore, the development recently of theories for the thermodynamic treatment of irreversible processes may open the way for a more wide-scale use of this powerful discipline in the study of biological problems.

Actually, naturally occurring processes are never reversible, so the reason for using irreversible thermodynamic theory to describe biological systems is that such systems are seldom at equilibrium. To these systems, classical thermodynamic theory does not apply; but for systems not too far from equilibrium, irreversible thermodynamics could well apply. This discussion will be pursued later in more detail.

Although the theory of irreversible thermodynamics would seem to apply to biological systems, it is impossible to determine to what extent it is valid without experimental verification. It would, therefore, seem reasonable to suggest a phenomenon which might take place in biological systems according to theory and results of experiments on non-biological systems and then seek experimental evidence of its taking place.

One finds in discussions of flow phenomena for both biological and non-biological systems that conditions of constant temperature throughout the system are almost universally assumed. In nature, this condition very rarely occurs. The unequal absorption of solar energy by different parts of a plant due to position or color cause temperature gradients. Also, sites where metabolism is occurring within plant cells may be at different temperatures from the surrounding material (Spanner, 1954). It is, therefore, of considerable interest to know what effect, if any, these temperature gradients have on the flow of substances through plant material.

With these ideas in mind, a study of the effect of temperature gradients on the flow of water in plant material was undertaken and the results were analyzed using the theory of thermodynamics of irreversible processes.

## REVIEW OF LITERATURE

Early observations

Thermo-osmosis, or the thermally driven flow of a liquid through a membrane, was first discovered and named by Lippmann (1907). His observations were made using a gelatine membrane with water as the liquid. Considerable flow was achieved, though with a rather large temperature gradient (about 80 centigrade degrees). The flow was from the cold side of the membrane to the hot side.

Aubert (1912) continued the work of Lippman using several different membranes with water and organic liquids as the permeating substances. He found that liquids flowed from cold to hot across some membranes and flowed from hot to cold across others. He was, however, unable to obtain a steady-state pressure difference across the membrane. He, therefore, attributed the effect to electro-osmosis due to the presence of impurities within the membranes.

Recent experimental work on thermo-osmosis across membranes

Steady-state thermo-osmotic effects were observed by Alexander and Wirtz, whose work is reviewed by Haase (1959). According to Haase (1959), Alexander and Wirtz were able to obtain thermo-osmotic flow of water across either cellophane or Goldschlägerhaut membranes. The direction of flow for the former was from hot to cold and for the latter was from cold to hot.

A rather complete treatment of the theory of thermo-osmosis across membranes is given by Haase (1959), and experimental work on thermo-osmosis

using several methods was presented by Haase and Steinert (1959). Some of their experiments will be discussed in more detail later. They used cellophane membranes and always observed flow from hot to cold.

Recent experimental work on thermo-osmosis  
in soils and other porous bodies

Aubert (1912) used porous material in studies of thermo-osmosis but was unable to detect any flow. Later, Derjaguin and Sidorenkov used a sintered-glass disc with water and other liquids. The resulting flow was surprisingly large according to Hutchison, Nixon, and Denbigh (1948), so their experiment was repeated by these three authors with similar results being obtained. The same results were achieved, however, when they replaced the sintered-glass disc with a solid glass disc. It was, therefore, concluded that the observed flow was due to thermal expansion rather than thermo-osmosis. Hutchison, Nixon, and Denbigh (1948) then constructed an apparatus in which the steady state liquid flux could be measured. They obtained flow initially, but their results were erratic and finally were shown to be due to impurities in the sintered-glass disc. They presented the theory of thermo-osmosis, stated the conditions under which non-negligible flows would occur, and concluded that thermo-osmosis through sintered-glass was negligible.

No attempt will be made to present a complete review of the rather extensive experimental work done on water movement in soils due to temperature gradients. References to this work may be found in a dissertation by Cary (1961). Several papers which are important to this study should, however, be mentioned because they contain important experimental and theoretical work.



A significant paper in which thermo-osmosis in soils was analyzed using irreversible thermodynamics was presented by Taylor and Cary (1960). The experimental results presented showed that water moved through a soil column from hot to cold. Experimental results of this nature had been obtained by earlier workers, but this was the first application of irreversible thermodynamic theory to thermo-osmosis in soil. The theory was introduced as a possible method of analyzing any system where simultaneous flows are occurring and experimental data were shown to agree, at least qualitatively, with the theory.

Work on the application of thermodynamics of irreversible processes to soils systems was continued by Cary (1961), and two important papers were published on the subject (Cary and Taylor, 1962a and 1962b). In these papers the theory was developed more completely, and the Onsager relations were verified for a soil system under the conditions present in the experiment. The theory was later extended to unsaturated soil systems (Taylor, 1963; Taylor and Cary, 1964) and applied to data obtained by Taylor and Cavazza (1954).

#### Application of irreversible thermodynamics to biological systems

The application of irreversible thermodynamics to biological systems has been the subject of several recent papers (Russell, 1960; Kedem and Katchalsky, 1958, 1961; Katchalsky and Kedem, 1962; and Bernhard, 1964). The systems usually treated are at constant temperature with water and solutes or electricity and ions flowing, although an irreversible thermodynamic treatment of water flow in biological systems not at constant temperature has been given (Spanner, 1954; Taylor, 1963).

Spanner (1954) suggests that temperature gradients in living tissue may be responsible for the active transport of water. He also presents a derivation of an equation to relate the transport of water by heat to the temperature dependence of the cell permeability to water. Using this equation and a typical value for the temperature dependence of the permeability, he calculates that a temperature gradient could produce a driving force for water in plant material equal to a water potential gradient of  $-13,200$  joules/kg/degree centigrade. He indicates that the negative sign means a pressure buildup on the low temperature side. Thus, according to Spanner's (1954) calculations, thermo-osmosis in biological systems may be of considerable importance; and flow occurs from hot to cold. No experimental evidence of thermo-osmosis in biological systems was presented.

In summary, thermo-osmosis has been observed in both soil and membrane systems and has been observed to occur either from hot to cold or cold to hot, depending on the membrane used. The occurrence of thermo-osmosis in biological systems has been proposed, but no experimental evidence has been given. Irreversible thermodynamic theory has been shown to apply to both soil and membrane systems.

#### The application of irreversible thermodynamics to thermo-osmosis

References on the history and development of thermodynamics of irreversible processes and its application to thermo-osmosis may be found in Hutchison, Nixon, and Denbigh (1948). The theory is given in several works (Prigogine, 1955; Denbigh, 1951; and Taylor, 1963). No attempt will be made to present a complete treatment of the theory; however,

some general remarks along with special applications to the problems presented in this thesis will be covered. The general remarks presented will be similar to the development in Morse (1964) and Taylor (1963).

Consider the system pictured in Figure 1, consisting of two reservoirs of a fluid, designated by ' and ", separated by a porous partition

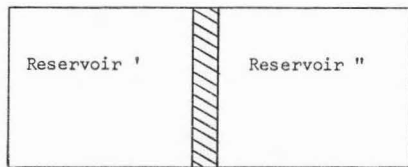


Figure 1. Isolated system consisting of reservoirs separated by a porous partition.

through which fluid may flow. If the system is in equilibrium, then the internal entropy,  $S' + S'' = S$ , will be a maximum. If the system is not in equilibrium, then according to the second law of thermodynamics, fluid and energy flow will occur in such a manner that the entropy will become a maximum. If the second law of thermodynamics is written with the internal entropy as a function of other variables, then the following equations are obtained:

$$dS' = \frac{1}{T'} dU' - \sum \frac{\mu_k'}{T'} dM_k' \quad [1]$$

$$dS'' = \frac{1}{T''} dU'' - \sum \frac{\mu_k''}{T''} dM_k'' \quad [2]$$

where  $U$  is the internal energy of the system,  $T$  is the temperature,  $\mu_k$  is the chemical potential of species  $k$ , and  $M_k$  is the mass of species  $k$ . The total entropy change can be written as the sum of the entropy changes

in each of the reservoirs

$$dS = dS' + dS'' = \Delta\left(\frac{1}{T}\right) dU' - \sum_{k=1}^n \Delta\left(\frac{\mu_k}{T}\right) dM'_k \quad [3]$$

where  $T$  is the average of  $T'$  and  $T''$ .

The rate of entropy production is obtained by taking the derivative with respect to time.

$$\frac{dS}{dt} = \Delta\left(\frac{1}{T}\right) \frac{dU'}{dt} - \sum_{k=1}^n \Delta\left(\frac{\mu_k}{T}\right) \frac{dM'_k}{dt} \quad [4]$$

Equation [4] is thus the sum of the products of the fluxes,  $\frac{dU'}{dt}$  and  $\frac{dM'_k}{dt}$ , and the thermodynamic forces  $\Delta\left(\frac{1}{T}\right)$ , and  $\Delta\left(\frac{\mu_k}{T}\right)$ , and can be written as

$$\sigma = \frac{dS}{dt} = J_U X_U - \sum_{k=1}^n J_k X_k \quad [5]$$

where the  $J$ 's are fluxes and the  $X$ 's are "forces."

For many systems which are close to equilibrium, the flux of material or energy can be written as a linear function of the "forces"

$$J_i = \sum_{k=1}^n L_{ik} X_k + L_{iu} X_u$$

$$J_u = \sum_{k=1}^n L_{uk} X_k + L_{uu} X_u$$
[6]

where the  $L$ 's are constants or functions relating the fluxes to the forces. Although existing flow equations are linear functions of the "forces," in many cases a number of the forces are neglected. Equations [6] indicate that flows may result not only from chemical potential gradients in a given species, but also from chemical potential gradients of other species or from energy gradients. The linked flow of material or energy will take place in a manner which will increase the entropy of the system. This determines the direction of the flows.

These principles are the basis of the study presented here. The study involves the flow of water through plant material due to heat flow. Since equations [6] are written in terms of energy flow instead of heat flow, a transformation is necessary. The appropriate equations can be written as (see Taylor, 1963, p. 2.6)

$$J_w = -L_{ww} \frac{(\Delta\mu_w)_T}{T} - L_{wq} \frac{\Delta T}{T^2} \quad [7]$$

$$J_q = -L_{qw} \frac{(\Delta\mu_w)_T}{T} - L_{qq} \frac{\Delta T}{T^2} \quad [8]$$

where  $(\Delta\mu_w)_T$  indicates the chemical potential at constant temperature, and w and q denote water and heat.

For systems where the linear approximation (equations [6]) holds and the units are properly chosen, Onsager's symmetry principle is valid and  $L_{wq} = L_{qw}$ .

Several experimental configurations are possible for obtaining  $L_{ww}$ ,  $L_{wq}$  or  $L_{qw}$ , and  $L_{qq}$ . Equation [7] will be of primary concern in this study because the ratio,  $\frac{L_{wq}}{L_{ww}}$ , is a measure of the relative importance of heat in the transport of water. This ratio is given the symbol  $Q^*$  and is called the heat of transfer. Where no linked transfer occurs,  $L_{wq} = 0$ , and  $Q^*$  is therefore zero. The units of  $Q^*$  are heat transferred per quantity of water, or joules per kilogram.

Possibly the simplest method for measuring  $Q^*$  is that used by Haase and Steinert (1959) in one of their experiments and by Taylor and Cary (1960). The apparatus is shown in Figure 2. It consists of two reservoirs separated by a porous plug or membrane. The reservoirs are maintained at different temperatures, and, in general, at different pressures.

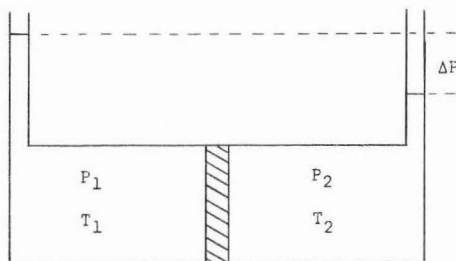


Figure 2. Apparatus for measuring the thermo-osmotic pressure difference.

The temperature difference can be read with thermometers and the pressure difference with water manometers. If both chambers contain pure water, then equation [7] can be written in terms of the pressure difference,  $\Delta P$

$$J_w = -L_{wW} v_w \frac{\Delta P}{T} - L_{wQ} \frac{\Delta T}{T^2} \quad [9]$$

where  $v_w$  is the specific volume of water at temperature  $T$ . If linked transfer occurs, then water will flow through the porous partition and a pressure difference will develop until  $J_w$  goes to zero. At  $J_w = 0$ , equation [9] can be solved for  $\frac{L_{wQ}}{L_{wW}}$  in terms of known quantities.

$$\frac{L_{wQ}}{L_{wW}} = Q^* = -v_w T \frac{\Delta P}{\Delta T} \quad [10]$$

The steady-state pressure and temperature differences are easily measured, and from these a value of  $Q^*$  can be obtained for the particular porous partition being used.

Although this method is simple, it has several undesirable features. First, it is not possible to use this apparatus to verify Onsager's symmetry principle because only the ratio  $\frac{L_{WQ}}{L_{WW}}$  is measured and not the value of each. Second, the system is always saturated since the water in the reservoirs and membrane is always under pressure.

In order to overcome these undesirable features, another type of apparatus was used by Cary (1961). A similar piece of apparatus was used by Haase and Steinert (1959); however, the analysis here will follow Cary (1961). The apparatus is shown in Figure 3.

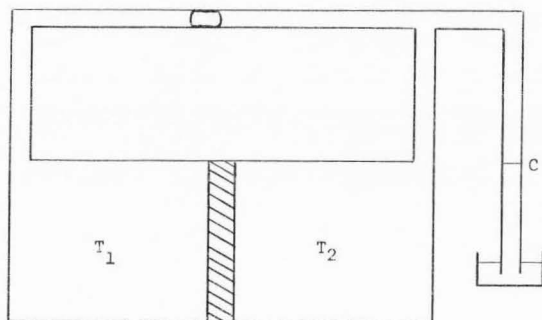


Figure 3. Apparatus for measurement of thermo-osmotic flow.

Again there are two chambers at different temperatures separated by a porous partition, but in this case the chambers are maintained at the same pressure by the mercury column, C, and connected by a capillary tube which contains a bubble so that the flow of water from one chamber to the other can be measured. The apparatus is also calibrated for heat loss so that the heat flux through the porous partition can be

measured. Thus it is possible to measure  $J_w$ ,  $J_q$ , and the temperatures. The chemical potential difference remains the same, so equations [7] and [8] can be solved simultaneously if data are taken at two values of  $T$ . The solution of the equations gives  $L_{ww}$ ,  $L_{wq}$ ,  $L_{qw}$ , and  $L_{qq}$ . With these values,  $Q^*$  can be calculated from  $\frac{L_{wq}}{L_{ww}}$ , and the Onsager principle can be tested from the relationship of  $L_{wq}$  to  $L_{qw}$ . The apparatus can be used for saturated or unsaturated systems by varying the height of the mercury column.

A similar method of analysis could be used on the thermo-osmotic pressure apparatus if the water column heights are measured as a function of time. At a given time,  $t_1$ , one is able to measure or calculate  $J_w$ ,  $J_q$ ,  $(\Delta u_w)_T$ ,  $\Delta T$ , and  $T$ ; and at a later time,  $t_2$ , similar values can be calculated or measured, so the equations can be solved for the  $L$ 's. If data are taken at several times, it is possible to check the validity of the application of the theory to the experiment by checking the  $L$ 's obtained at one time against the  $L$ 's obtained at another time. Since steady-state conditions are assumed, the  $L$ 's should be constant with time. If this is not true, then either the assumptions made in applying the theory to the system are not valid, or the measurements made are in error.

A method used to determine the transport of water by heat in continuous, unsaturated systems was applied by Taylor and Cavazza (1954) to unsaturated soil columns. The treatment of this type of system using irreversible thermodynamics was presented by Taylor (1963) and Taylor and Cary (1964). The experimental apparatus consists of a chamber in which a sample may be placed and subjected to a thermal gradient.



The rate of flow of moisture from one area to another as a function of time can be measured by sampling as was done by Taylor and Cavazza (1954) or by neutron attenuation.<sup>1</sup> From these measurements,  $J_w$  can be calculated. The chemical potential at constant temperature can be determined by tensiometers in the sample, by sampling for chemical potential measurements, or by obtaining a functional relationship between water content and chemical potential. Again the  $L$ 's can be calculated by varying the parameters of temperature or time and obtaining the data to solve equations [7] and [8] simultaneously. The  $L$ 's are, in general, functions of moisture content or moisture potential, so this must be kept in mind in making these calculations.

In many cases, a better method is to leave the sample in the apparatus until a steady-state moisture distribution is achieved. At this time, the chemical potential is determined at several places in the sample, either in place or by sampling. Equation [7] is then solved for  $\frac{L_{wg}}{L_{ww}}$  with  $J_w = 0$ . This gives

$$\frac{L_{wg}^a}{L_{ww}^a} = Q^{a*} = \frac{-T(\Delta\mu_w)_T}{\Delta T} \quad [11]$$

The "a" indicates apparent transfer coefficients which are valid only for specified conditions of water content and temperature. The apparent heat of transfer,  $Q^{a*}$ , is often designated by  $\beta$  (see Taylor, 1963; Taylor and Cary, 1964).

The value of  $Q^*$  obtained using any one of these methods should be equal to the value obtained using another method if membrane conditions,

---

<sup>1</sup>This method was reported to the author in a personal communication with Glendon Gee, Department of Soils, Washington State University.

water potential, and temperature conditions remain constant from one experiment to the next. Haase and Steinert (1959) found that the variation from one method of measurement to another was no greater than the variation from one sample of material to another. The determining factor in selecting from among these experimental procedures should be, therefore, the feasibility of using that type of apparatus with the experimental material in question. The last method mentioned may give a better measurement of what is happening in nature, because saturated systems are encountered less frequently than are unsaturated systems in soil-plant-water studies. However, the term, unsaturated, loses its meaning when applied to plants in the same sense in which it is applied to soils; and since the analysis was developed for soils systems, a somewhat different approach may be required for plants. In any case, any approach mentioned should give valid information on the appropriateness of the theory in explaining the observations and the relative magnitude of thermally driven water flow.

Type of system necessary for non-zero values of  $Q^*$

The experimental materials reviewed to this point indicate that for a given system  $Q^*$  may be positive, negative, or zero. Positive values indicate flow toward the hot side of the membrane, negative values indicate flow toward the cold side of the membrane, and zero values, of course, indicate no interaction between the flow of heat and the flow of water. If one assumes that the "thermo-osmosis" observed by Lippmann (1907) and Aubert (1912) was actually electro-osmosis as Aubert suggested, then the only experimentally observed positive values of  $Q^*$

were obtained by Alexander and Wirtz (reported in Haase and Steinert, 1959) for water movement through a Goldschlägerhaut membrane, and Denbigh and Raumann (1951) for thermal diffusion of some gases through rubber membranes. Negative  $Q^*$  values were obtained by Haase and Steinert (1959) for cellophane membranes and by Taylor and Cary (1960) and Cary (1961) for soils. Zero  $Q^*$  values were obtained by Aubert (1912) for plugs of porous material and by Hutchison, Nixon, and Denbigh (1948) for sintered-glass plates. The experimental results, therefore, apparently depend on the nature of the membrane and the properties of the fluid being used. Two questions thus present themselves: Under what conditions might one expect thermo-osmosis to occur? And is it possible to predict the direction of the flow if the properties of the fluid and of the membrane are known?

The conditions under which thermo-osmosis may be expected to occur are discussed by Hutchison et al. (1948). Their conclusion is that thermo-osmosis occurs in systems which have non-zero  $Q^*$  values. They suggest that thermo-osmosis may occur when the permeating fluid is more soluble in the membrane at one temperature than at another, thus causing a concentration gradient within the membrane.

Spanner (1954) went much further in explaining the conditions for non-zero  $Q^*$  values. Consider the system shown in Figure 4 consisting of two reservoirs filled with water initially at constant temperature separated by a porous body or membrane. A pressure difference between the reservoirs causes water to flow from one reservoir to the other through the partition. If the pores in the partition are large enough to allow bulk flow of water, then the molecules passing from one chamber

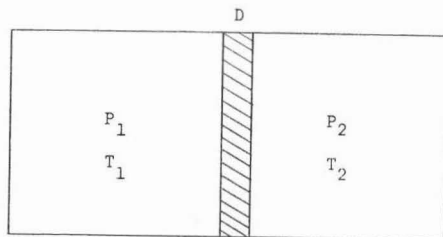


Figure 4. System for demonstrating the simultaneous flow of water and heat. System consists of two water reservoirs separated by a porous partition, D.

to the other will have a distribution of energies similar to the distribution of energies within the bulk liquid. However, let us assume that the pores become smaller and approach the intermolecular distance for water molecules. Since the higher energy molecules will achieve a greater number of collisions with the membrane than the lower energy molecules, the probability of a high energy molecule passing through the membrane is greater than the probability for a low energy molecule. Since more high energy molecules are passing through the membrane, the reservoir from which the water is flowing will become cooler, and the reservoir into which water is flowing will become warmer. With this type of system, the value of  $Q^*$  depends upon the effectiveness of the membrane as a "sieve" to separate low energy molecules from high energy molecules.

Although this illustration has been constructed to show that a pressure difference may cause a temperature difference for non-zero values of  $Q^*$ , the inverse is also simple to describe. If a membrane separates two reservoirs at different temperatures, then flow should

occur from hot to cold if the membrane is able to "tell the difference" between "hot" and "cold" molecules. This is because relatively more "hot" molecules will enter the membrane than "cold" ones, and a concentration gradient will be built up within the membrane. If the membrane is unable to act as a "sieve" to separate "hot" and "cold" molecules, then no thermo-osmosis should occur.

A more mathematical treatment is given by Bernhard (1964). Consider the system described in Figure 4. For this system, equations [6] become

$$J_w = L_{ww} \Delta\left(\frac{\mu_w}{T}\right) + L_{wu} \Delta\left(\frac{1}{T}\right) \quad [12]$$

$$J_u = L_{uw} \Delta\left(\frac{\mu_w}{T}\right) + L_{uu} \Delta\left(\frac{1}{T}\right) \quad [13]$$

In the stationary state,  $J_w$  goes to zero; and from equation [12],

$$\frac{\Delta\left(\frac{\mu_w}{T}\right)}{\Delta\left(\frac{1}{T}\right)} = - \frac{L_{wu}}{L_{ww}} \quad [14]$$

Now if the relation

$$\Delta\left(\frac{\mu_w}{T}\right) = \frac{v_w}{T} \Delta P + h_w \Delta\left(\frac{1}{T}\right) \quad [15]$$

is used and both numerator and denominator of the left-hand side of equation [14] are divided by  $\Delta\left(\frac{1}{T}\right)$ , the following will result

$$\frac{v_w \Delta P}{T \Delta\left(\frac{1}{T}\right)} + h_w = - \frac{L_{wu}}{L_{ww}} \quad [16]$$

where  $h_w$  is the specific enthalpy of the water.

For the case illustrated by Figure 3, that of a pressure gradient but no temperature gradient between the reservoirs, equations [12] and [13] can be solved simultaneously to give

$$\frac{J_u}{J_w} = \frac{L_{uw}}{L_{ww}} = \frac{L_{wu}}{L_{ww}} \quad [17]$$

if the Onsager symmetry principle holds. Equation [17] may now be substituted into [16] to obtain the relation

$$\frac{\Delta P}{\Delta(\frac{1}{T})} = \frac{T}{v_w} (h_w - \frac{J_u}{J_w}) \quad [18]$$

For bulk transfer of water, or free diffusion, the energy transferred per unit mass of water, or  $\frac{J_u}{J_w}$ , is just equal to the enthalpy of the water, making the term in parentheses in equation [18] equal to zero. However, if the membrane is selective and passes more high energy than low, the energy transferred per unit mass of water is not equal to the enthalpy. This is because the enthalpy of a characteristic of a representative sample of the water in the reservoirs; whereas on the average, higher energy molecules are selected for transport by the membrane. The difference between the enthalpy and the energy transported by the water through the membrane is the heat of transfer,  $Q^*$ . Substituting  $Q^*$  for  $(h_w - \frac{J_u}{J_w})$ , writing  $\Delta(\frac{1}{T}) = -\frac{\Delta T}{T^2}$ , and rearranging terms in equation [18] gives equation [10].

#### Membrane models and their relationship to $Q^*$ values

Several examples may be given of systems which pose energy barriers of the type necessary for thermo-osmosis. Possibly the simplest is a system where water must enter the vapor phase to pass from one area to another. The latent heat of vaporization is an energy barrier which can

be crossed only by those molecules with sufficiently high energies. Thus, an air gap is very selective and gives rise to  $Q^*$  values which are about equal to the height of the energy barrier or activation energy (Spanner, 1954; Cary, 1965).

Two other membrane models have been mentioned which would be expected to give non-zero values of  $Q^*$ . One is a membrane which contains pores of approximately inter-molecular dimensions, and the other is a membrane which is either hydrophylic or hydrophobic so that a relatively large activation energy is required either to enter the membrane or to leave it.

It is not difficult to find "membranes" in nature which correspond to these models. For instance, one would expect some thermo-osmosis to take place as vapor flow in unsaturated soils (Cary and Taylor, 1962a and 1962b). Liquid flow in soils is somewhat more difficult to explain, but it also involves the consideration of activation energies (Cary, 1965).

Water movement in plants takes place across cell membranes and through xylem tissue. Flow within the xylem probably takes place in the form of continuous streams of water extending the length of the xylem (Meyer, et al., 1960). The cells of the xylem tissue form capillary tubes which are large in relation to the intermolecular dimensions of water. The largeness of the capillaries is confirmed by data obtained by Jensen (1961) on the resistance and  $Q_{10}$  values for water flow through intact tomato and sun flower plants as compared to flow through stems only. From these observations and the considerations of energy sieving already presented, thermo-osmosis might not be expected to occur in xylem tissue.

Water flow across plant membranes is considerably more complicated, and some understanding of the nature of the membrane would be helpful in determining how effective it might be as a "sieve" to separate molecules of various energies.

Since water flowing through plant tissue would encounter primarily the plasmalemma and the tonoplast, these are the membranes of interest in this study. They are generally thought to consist of two layers of lipid sandwiched between an outer and an inner layer of protein (Giese, 1962; Harris, 1960; Davson and Danielli, 1943). If one assumes that some areas of lipid are exposed (Giese, 1962), then a water molecule passing through the cell membranes might encounter an energy barrier similar to that pictured in Figure 5.

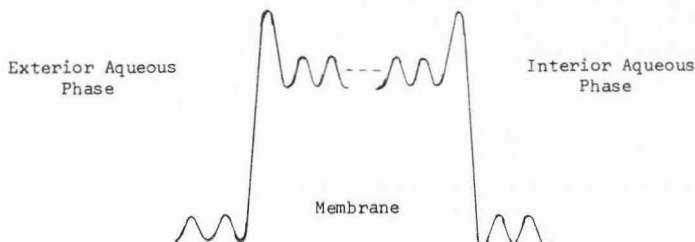


Figure 5. System of potential energy barriers encountered by water moving through a lipid membrane (adapted from Danielli, 1952).

The initially high energy required for a water molecule to enter the membrane is due to the energy required to break the hydrogen bonds with other water molecules and to form a pore in the hydrophobic lipid. The



resistance to movement through the membrane is quite high since cohesive forces between lipid molecules must be overcome in order to continue the pore in the membrane. A final, relatively high, energy barrier is encountered in the surface tension forces of the lipid. From here, the movement of the molecule from the membrane into the interior aqueous phase presents no problems since new hydrogen bonds are formed.

A later membrane model is presented by Danielli (1954). He retains the same "sandwich" structure just described, but postulates the existence of "pores" or continuous patches of protein extending through the lipid portion of the membrane as shown in Figure 6. These pores were suggested to account for passage of water and other small molecules through the membrane at a faster rate than could be accounted for using a pure lipid model. The energy barriers encountered by a water molecule passing through such a pore would be just opposite from those described for a lipid membrane. Dainty and Ginzburg (1964) suggest that the high activation energies for water movement through these pores indicate that the water has more "structure" in the pores than does bulk water. This would indicate a system of potential energy barriers for a molecule crossing a membrane via a polar pore resembling that pictured in Figure 7. The initial potential energy drop is due to hydrogen bonding with the proteins, this being more stable than the water to water bonds. Resistance to flow is encountered as the molecule passes through the membrane because hydrogen bonds must continually be broken in order for the molecule to progress. These bonds seem to account, in large part, for the anomalous  $Q_{10}$  values for the passage of small molecules through membranes reported by Danielli (1952). The major barrier encountered by a water molecule passing through a polar pore would be

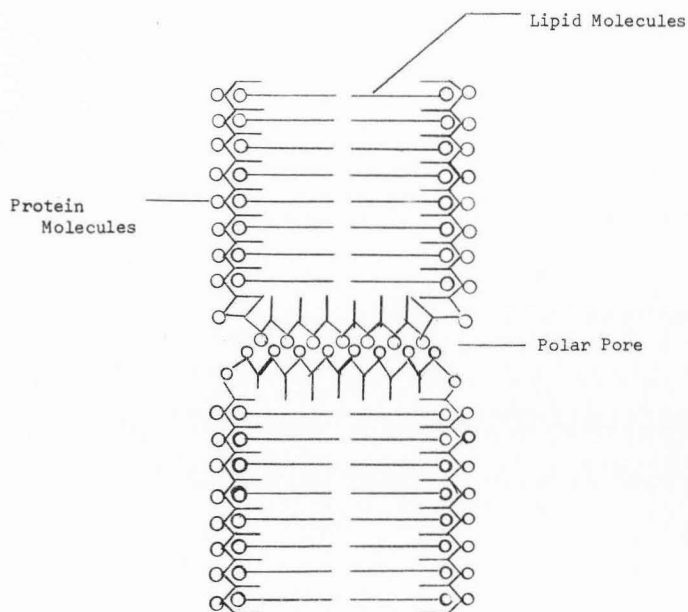


Figure 6. Diagram of a polar membrane pore (from Danielli, 1954).

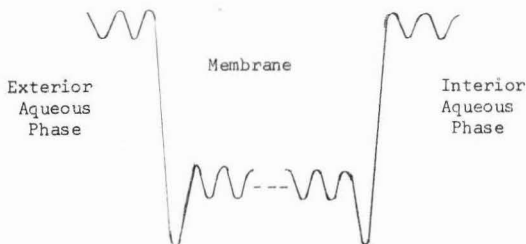


Figure 7. Possible system of potential energy barriers encountered by a water molecule passing through a polar pore.

the re-entry into the internal aqueous phase, since rather stable bonds would have to be broken.

The two models discussed furnish some possible insight into the mechanisms involved in thermo-osmosis across plant membranes. If the first model accurately represents plant membranes, water should flow from hot to cold when plant tissue is subjected to a temperature gradient. This flow would result because the higher energy molecules would be selected and transported by the membrane whereas low energy molecules would be held back. Membranes represented by the second model would give rise to the opposite effect. The potential "ditch" presented by the membrane would tend to select low energy molecules, thus causing water to flow from a cold reservoir to a hot reservoir (see Spanner, 1954). Thus it is possible to explain either positive or negative values of  $Q^*$  by postulating membrane properties similar to either the first model or the second. It might, therefore, be possible, as Bernhard (1964) suggests, to determine the properties of membranes and the mechanism of flow through them from thermo-osmosis data.

### Conclusions from the literature review

1. Reliable thermo-osmosis experiments have been conducted using water with cellophane membranes, animal membranes (Goldschlägerhaut), soils, and sintered-glass plates. Water moved from the hot side of the system toward the cold side for cellophane membranes and soils. No significant water movement occurred through sintered-glass, and water moved from the cold side of the membrane to the hot side for animal membranes.

2. The theory of thermodynamics of irreversible processes has been successfully applied to systems exhibiting thermo-osmosis. The systems seem to be adequately described by this theory.

3. Thermo-osmosis would only be expected to occur in cases where the membrane acts as a sieve which passes molecules of one energy more readily than molecules of another energy.

4. Plant cell membranes may work well as "energy sieves," although saturated xylem tissue may not. Thus, thermo-osmosis may occur in plant cells and not in saturated xylem tissue.

5. Flow may occur through plant membranes, either from hot to cold or from cold to hot depending on the properties of the plant membranes.

## EXPERIMENTAL METHODS

Preliminary studies

There were three objectives in carrying out preliminary studies on thermo-osmosis in plant tissue. First, since experiments had previously been conducted only with non-living material, it was necessary to determine whether or not the same apparatus would be useful in determining the thermo-osmotic properties of living plant material. If the apparatus was not adequate for the present studies, then the preliminary work was to determine whether thermo-osmosis occurs in plant tissue and what measurements would be necessary to determine the magnitude of the effect. Third, it was desirable to obtain information as to which type of plant material would be most suitable for the study.

With these objectives in mind, the method of Taylor and Cavazza (1954) seemed best suited to the study. Samples of potato tuber (*Solanum tuberosum* L.) and sugar beet root (*Beta vulgaris* L.) were used for the experiment material. It was immediately apparent that several modifications in the apparatus would be necessary. The main modification was to use much smaller samples than were used in the soils studies. Since living plant material would deteriorate within a day or less under the conditions of the experiment, it was hoped that with smaller samples equilibrium could be reached more rapidly.

The apparatus used is shown in Figure 8. The sample chamber was constructed from a piece of lucite shaft 6.3 cm in diameter and 7 cm long. A hole 2 cm in diameter was drilled through the shaft and threaded for 1 cm on each end. Thermocouple holes, 0.1 cm in diameter, were drilled

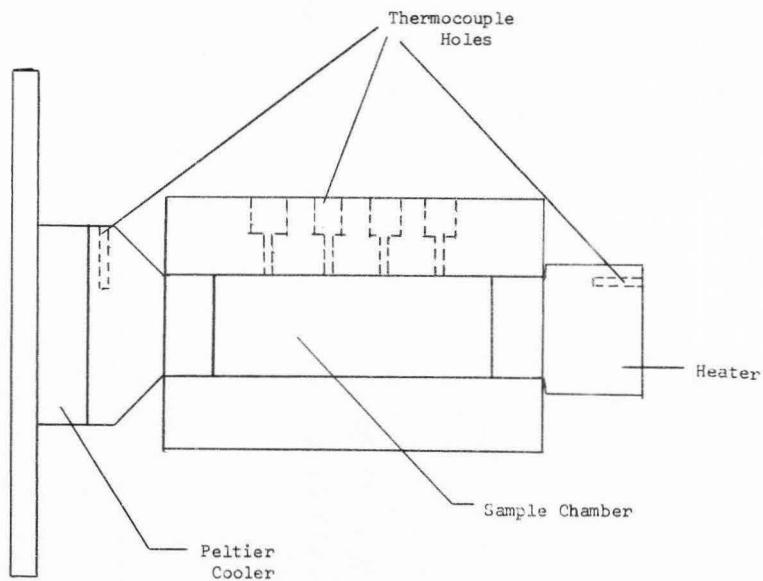


Figure 8. Apparatus used in preliminary thermo-osmosis studies.

at 2, 3, 4, and 5 cm from the end into the sample chamber. The tops of the holes were enlarged to 0.6 cm diameter to a depth of 1 cm to receive the small rubber stoppers in which the thermocouples were mounted. The heater was constructed of brass and threaded to screw into the chamber. The protruding end was wrapped with several layers of 30 B & S gauge enameled constantan wire and electrical tape. A hole was drilled in the center of the heater so that the temperature could be determined with a thermocouple.

A thermoelectric cooler<sup>1</sup> was used as a refrigerator at the cold end of the sample. A brass piece was machined to bolt to the cooler and screw into the cylinder. The other side of the cooler was bolted to a copper plate onto which copper coils had been soldered. Cooling water was circulated through the copper coils to cool both the hot side of the thermoelectric element and the air bath in which the apparatus was contained. Six iron-constantan thermocouples were used to determine the temperature at various places in the sample. One was mounted in each brass end piece, and four were placed in the sample. The temperatures were recorded on a multipoint thermocouple recorder.<sup>2</sup>

The entire apparatus was enclosed in a styrofoam box which served as a constant temperature air bath. The bath was controlled to about  $\pm 0.1$  centigrade degrees. A squirrel cage blower mounted in the lid of the box provided air circulation. Variable transformers were used to adjust the current flowing through the heater and the cooler and thus control the heater and cooler temperatures.

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<sup>1</sup>General Electric Corporation, Semi-conductor Division, Youngwood, Pennsylvania. Type 814 F.

<sup>2</sup>Leeds and Northrup Co., Philadelphia, Pennsylvania. Speedomax G recorder.

The temperature gradient along a potato sample was first determined. A non-linear gradient was always obtained; however, this became more nearly linear when the potato was wrapped in aluminum foil to prevent heat loss by radiation. The bath temperature was controlled at 20 C, and the hot and cold ends were at about 30 C and 10 C respectively. A representative temperature vs. distance curve is shown in Figure 9.

Cylindrical potato plugs 2 cm in diameter and 5 cm long were cut and placed in the apparatus. These were subjected to thermal gradients of about 4 centigrade degrees per cm for varying lengths of time. When a run was completed, the sample was removed from the chamber and cut into one cm lengths. These were weighed and dried in a vacuum oven at 70 C for 24 hours. The dried samples were then reweighed and the percent water was determined. Data obtained using this method showed a water content gradient in the tissue, but the variability from sample to sample was quite large. The reason for at least some of this variability seemed to be associated with variations in turgidity from sample to sample. The samples were, therefore, soaked in manitol or carbowax 400 solutions for a number of hours before the run was started. The variability remained high, however, even after this treatment; and the procedure was later discontinued.

From the data obtained, curves relating the water content of the sample to the temperature were constructed. Figures 10, 11, and 12 show this relationship for selected runs. The time the sample was in the apparatus is shown on each figure. Although these figures are constructed using some of the smoothest moisture gradients obtained, almost all runs showed a distinct buildup of moisture on the cold end of the sample and a loss of moisture from the hot end. In general, wetter samples showed



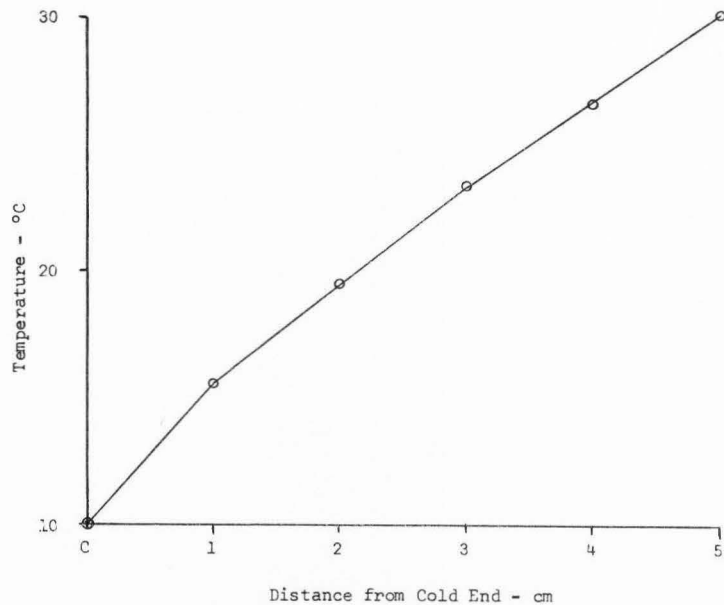


Figure 9. Temperature gradient for preliminary apparatus. The sample used is from a potato tuber.

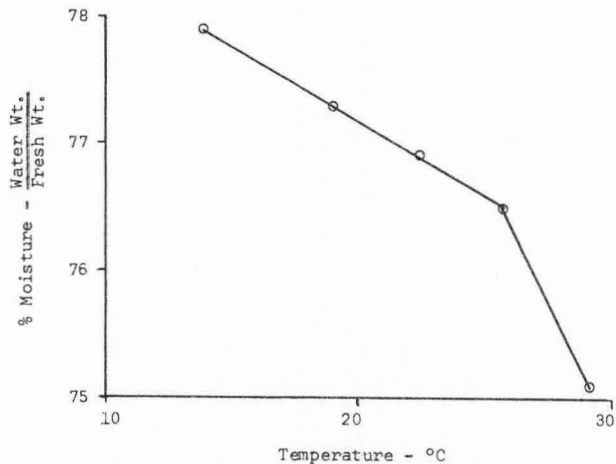


Figure 10. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg solution of carbowax 400 and was subjected to the temperature gradient for 18 hours, 33 minutes.

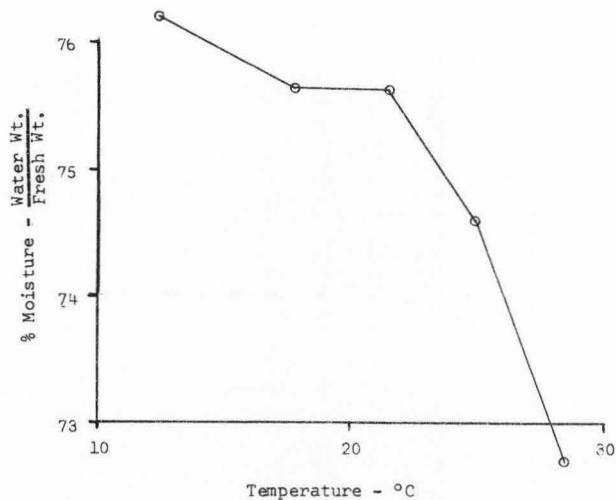


Figure 11. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg solution of carbomax 400 and was subjected to the temperature gradient for 24 hours, 45 minutes.

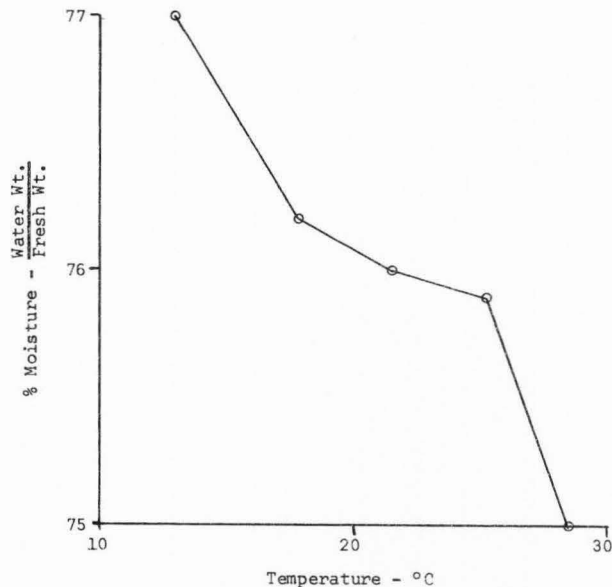


Figure 12. Curve showing water content distribution as a function of temperature for a potato tuber sample in the preliminary apparatus. The sample was soaked in a 1400 joules/kg carbowax 400 solution and was subjected to the temperature gradient for 24 hours, 14 minutes.

less movement than drier samples. This apparently results from the cold end becoming saturated in wet samples, leaving no place to which the water could move. The moisture content of the cold end was often at about 80% moisture, and this was also determined to be the approximate moisture percentage of potato samples soaked in water.

Samples of sugar beet root were also used in the apparatus just described. The results were similar to those obtained using potato, but sugar beets deteriorated less rapidly than potatoes. Potatoes could only be placed in the apparatus for about 24 hours without showing signs of deterioration. Sugar beets would last about twice that long. The signs of deterioration referred to here were only those which could be detected visibly or from smell. Chemical changes no doubt took place earlier, but no tests were made.

Two things were learned from the preliminary experiment. First, it was shown that water moved in plant material under the influence of a temperature gradient. Second, this phenomenon seemed to occur in both potatoes and sugar beets. Potatoes were preferred, however, because the tissue was more homogeneous. It would be difficult to tell which tissue might be involved in the transport of water in sugar beets because a sample large enough for use in this apparatus would include xylem, phloem, and storage tissue.

Several problems became apparent in these studies. A comparison of Figures 11 and 12 shows that two replications treated exactly alike give rather different results due to variability from sample to sample. It was originally thought that this resulted from the sample being too large for equilibrium to be reached in the twenty-four hours allowed. Since visible deterioration of the potato tuber tissue occurred within

24 hours, longer equilibrium times could not be tolerated. It, therefore, seemed necessary to use a smaller sample. Another problem encountered came in the solution of equation [11]. To solve this equation, one must be able to obtain values of  $(\Delta\mu_w)_T$ . If one is able to obtain a functional relationship between the water content of the sample and  $(\Delta\mu_w)_T$ , then from this and the water content values in Figures 10, 11, and 12, values of  $(\Delta\mu_w)_T$  can be calculated. Several attempts were made to obtain such a relationship for potato tuber tissue, but the variability from sample to sample was too large to yield any meaningful results. This indicated the need for a direct measurement of the chemical potential gradient along the sample. Some such measurements were made during the preliminary experiment using Peltier thermocouple psychrometers which were available; however, readings were only reliable to about 100 joules/kg, and many of the gradients were smaller than this. It was, therefore, necessary to improve the technique for measuring water potential in plant samples so that readings accurate to at least 10 joules/kg could be made.

The apparatus which was developed for this is described by Campbell, Zollinger, and Taylor (1965). It consisted of a sample changer with which a thermocouple psychrometer could be used. With this equipment, water potential measurements could be made with the desired accuracy.

#### Experimental determination of the apparent heat of transfer

Using the knowledge obtained in the preliminary experiment, an apparatus was constructed to measure the apparent heat of transfer. The apparatus is shown in Figure 13. It consists of two stirred constant temperature water baths separated by a removable lucite partition 1.2 cm

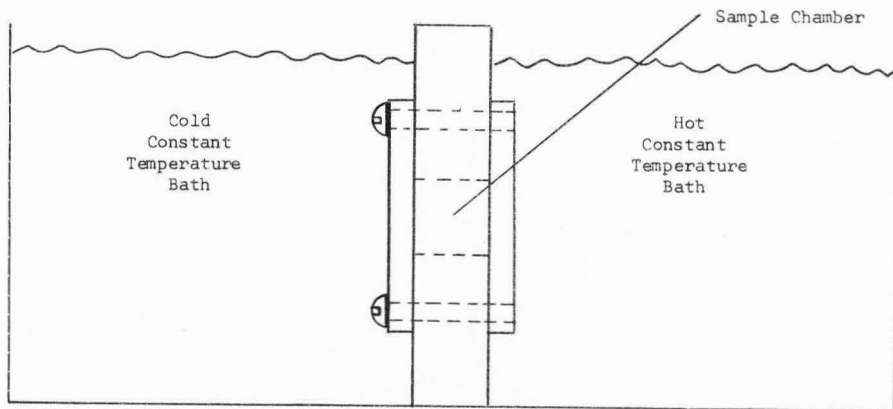


Figure 13. Apparatus for determining the apparent heat of transfer.

thick. Two 1-cm diameter sample chambers were drilled into the partition and covered with brass pieces which were held in place by four screws. Vacuum grease provided a good enough seal so that when the brass pieces were screwed down tight, no water entered the chambers from the constant temperature baths.

The bath temperature was controlled to about  $\pm 0.25$  centigrade degrees. A ten degree gradient was always used. The baths were either set at 10 and 20 C or 20 and 30 C.

Samples were cut from a potato tuber using a 1 cm diameter cork borer. These were washed and soaked in manitol or carbowax 400 solutions for one hour. The samples were then blotted, placed in the sample chambers, and cut to the proper length. The brass plates were screwed into place, and the apparatus was placed in the gradient bath for about fourteen hours. At this time the samples were removed, cut into slices .2 cm thick, and the water potential of each slice was determined using a sample changer and thermocouple psychrometer (Campbell, Zollinger, and Taylor, 1965).

Considerable difficulty was experienced in cutting the potato tuber samples into six slices of equal size. Several methods were tried, none of which was completely satisfactory. The best slices were obtained using a hand microtome to cut the slices before the gradient was applied. Several runs were made using this technique. It was discontinued because some of the data seemed to indicate flow discontinuities in the tissue at some of the cuts.

Attempts were made to modify the microtome to cut the tissue after it was subjected to the temperature gradient. These were never completely satisfactory either, because the samples couldn't be clamped in



the microtome. However, it was usually possible to get five good discs out of six. This was the method used for the data to be presented. Other methods were tried, including bolting five razor blades together with the proper spacing, and a chopping technique described by Templeton (1961). These all worked about equally well and usually no better than the hand microtome. A high humidity box was used when the samples were cut and loaded into the chambers so that water loss would be reduced.

The data obtained are presented in Figures 14 and 15. All points are the average of four readings except the two coldest points on Figure 15. No data were obtained on the coldest point for Figure 14. The reason for the loss of these points was the difficulty experienced in cutting the samples. Only full discs which were about 0.2 cm thick were used for the data.

Values of  $Q^*$  or  $\beta$  can be calculated from equation [11] using the data from Figures 14 and 15. These are presented in Table 1. More data

Table 1. Apparent heat of transfer for several values of temperature ( $T$ ), water potential ( $\psi$ ), and chemical potential gradient  $(\Delta\mu_w)_T$ . Values of  $T$ ,  $\psi$ , and  $(\Delta\mu_w)_T$  were taken from Figures 14 and 15.

$T$ °K	$\psi$ joules/kg	$(\Delta\mu_w)_T$ joules/kg	$\beta$ joules/kg
286.5	1348	15	2527.9
288.2	1373	36	6103.1
289.9	1407	33	5627.5
291.6	1442	36	6175.1
294.9	1327	11	1908.2
296.5	1338	11	1918.5
298.2	1356	24	4209.9
299.9	1385	34	5998.0
301.6	1421	38	6741.6

$\Delta T = 1.7$

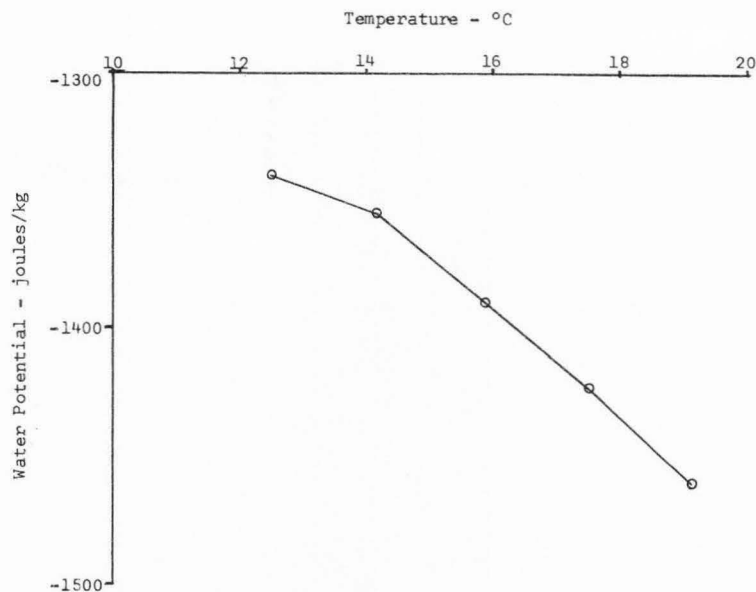


Figure 14. Water potential distribution as a function of temperature in a 1.2 cm long, 1 cm diameter potato sample. Sample was subjected to an 8.3 centigrade degree/cm temperature gradient for about 14 hours.

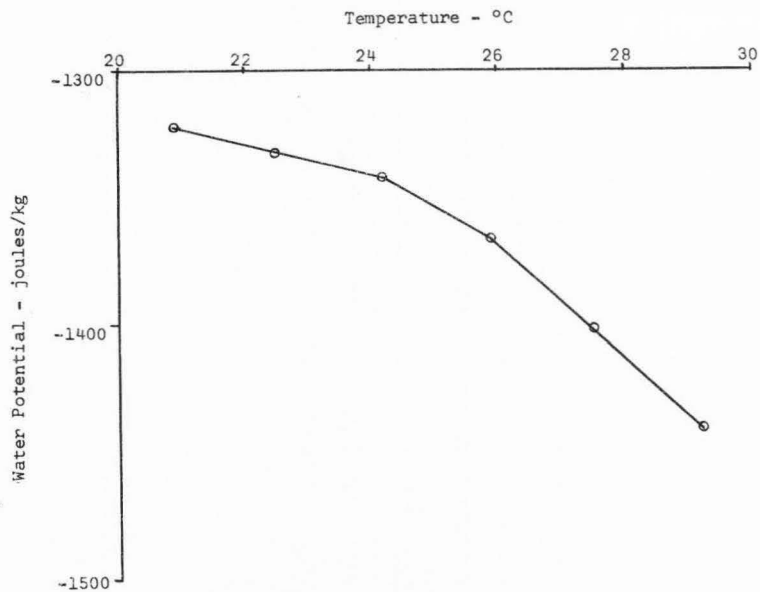


Figure 15. Water potential distribution as a function of temperature in a 1.2 cm long, 1 cm diameter potato sample. Sample was subjected to an 8.3 centigrade degree/cm temperature gradient for about 14 hours.

were taken that are shown in Figures 14 and 15 with generally similar results. However, some runs gave data which were exactly the opposite of that shown here. This indicated that although thermo-osmosis was probably occurring, other processes were also taking place which modified the results. Two reasonable possibilities seemed to be (1) that water and/or heat flow were linked with solute flow so that solutes moved within the tissue, and (2) chemical reactions were taking place within the tissue which caused an increase or decrease of water potential in the tissue. Either possibility indicated the need for the measurement of a greater number of variables and the use of more equations to describe the system. Rather than try to make the other measurements necessary to completely describe the system, a different experimental approach was tried.

Determination of  $Q^*$  from thermo-osmotic  
pressure difference and thermo-osmotic  
flow

The experiments already mentioned seemed to indicate that meaningful measurements could be made only for short periods of time after the tissue was subjected to the treatment. This is borne out by the work of Roberson (1964) who showed a decrease with time in the water permeability of root tissue which was held in unaerated water. The difficulties involved in aerating tissue and at the same time measuring water movement through it seemed to be great, and it was not known that aerated tissue which had been cut from potato tubers would give results different from unaerated tissue. Roberson's data (1964) indicated, however, that changes were small within about the first two hours, so it seemed most desirable to construct an apparatus and use a method of

analysis which would give the required results within the first two hours after the sample was placed in the chamber.

The apparatus used for this study is shown in Figure 16. It was constructed to fit in the gradient bath which was used in the "apparent heat of transfer" study. The manometers were of 0.1 cm I.D. glass tubing and were mounted in rubber stoppers so that they could be removed to fill the reservoirs. The cylindrical sample chamber was 3.8 cm in diameter and 1.2 cm long.

A sample was prepared by machining a potato to 3.8 cm diameter using a metal lathe, and cutting an "O" ring groove 0.4 cm deep in it. A slice 1.2 cm long containing the "O" ring groove was cut from the potato and washed. The "O" ring was then coated with vacuum grease and put in place, and the sample was placed into the chamber. The reservoirs were screwed on and the apparatus filled with water. The water level in the manometers could be adjusted by inserting the rubber stoppers the desired distance.

The evolution of gas from respiration was a problem in some of the earlier experiments. It was found that if the reservoirs were subjected to a vacuum after they were filled with water, air was removed from the system and the evolution of gas was negligible for about 12 hours. This was long enough to obtain the necessary data.

The assembled apparatus was placed in the gradient bath which was set to control at 15 and 25 C. The water column heights were measured with a cathetometer at time intervals of 15 minutes. The difference in column height as a function of time for ten runs is presented in Figures 17 through 26. The figures show  $\Delta h$  positive when the cold side manometer is highest and  $\Delta h$  negative when the hot side is highest. Initially the

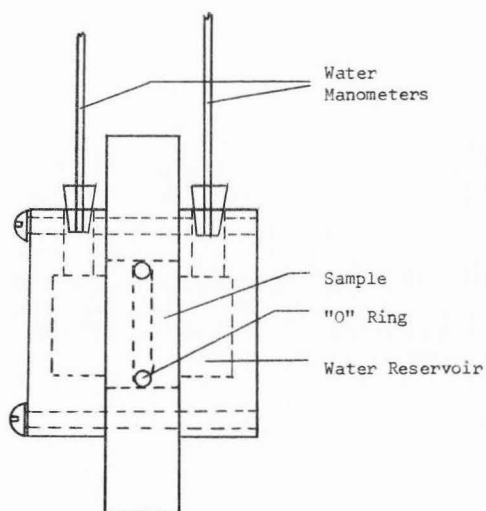


Figure 16. Apparatus for measuring thermo-osmotic flow and thermo-osmotic pressure difference.

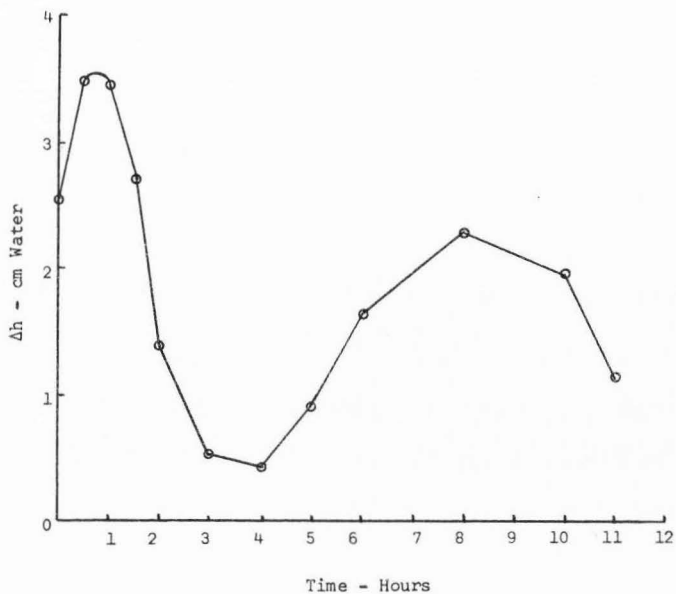


Figure 17. Pressure difference vs. time for a section of potato tuber which is subjected to a temperature gradient of 6.25 centigrade degrees/cm. Positive values of  $\Delta h$  indicate the pressure is highest on the cold side.

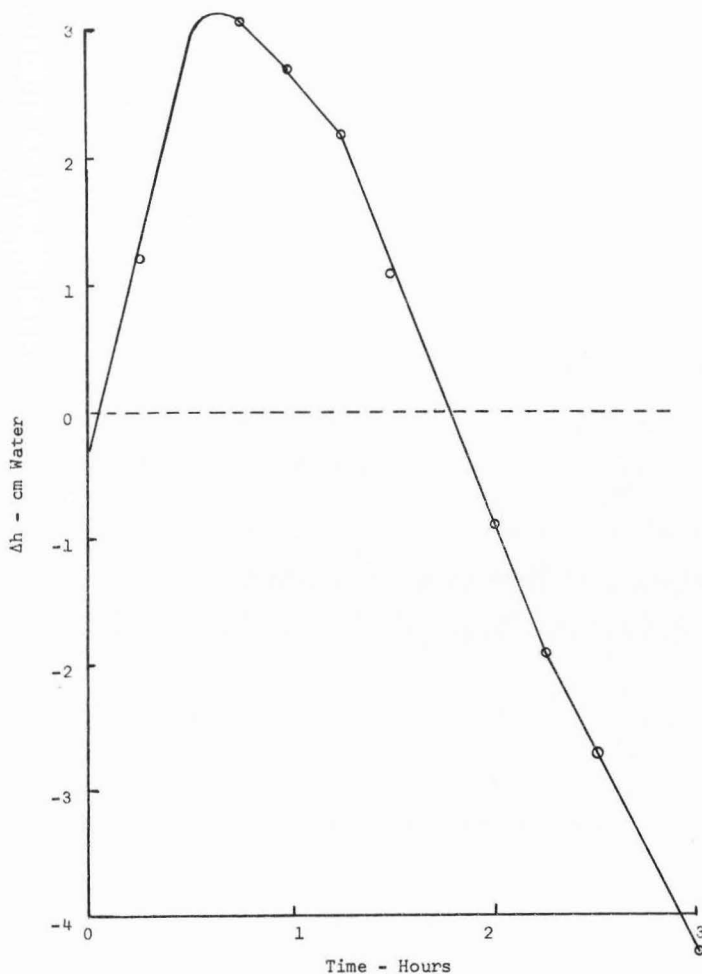


Figure 18. Pressure difference vs. time for a section of potato tuber which was subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate the pressure is highest on the cold side.



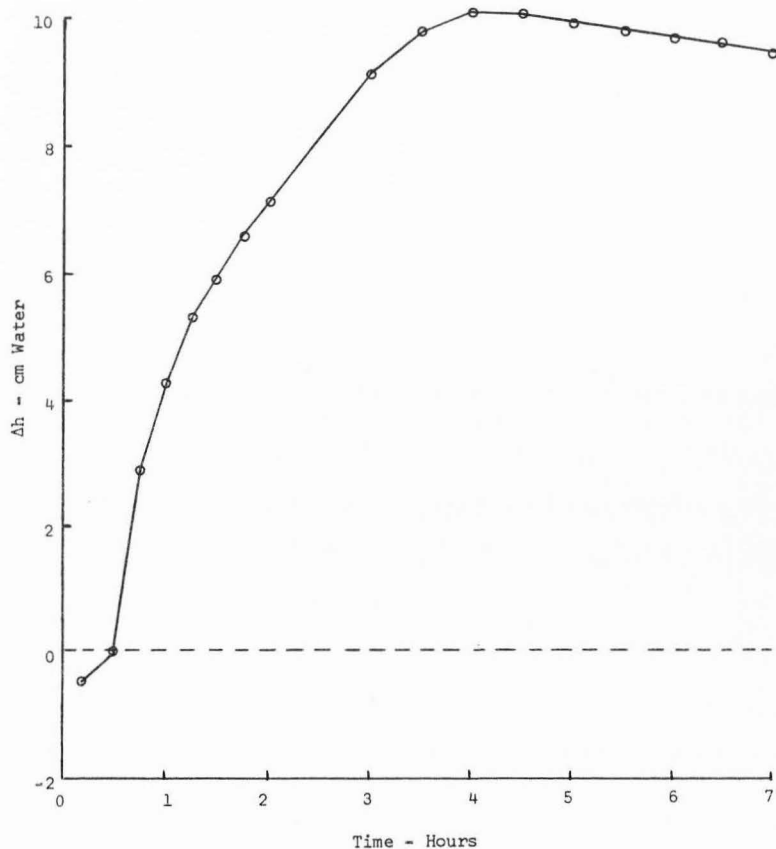


Figure 19. Pressure difference vs. time for a section of potato tuber which was subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate the pressure is highest on the cold side.

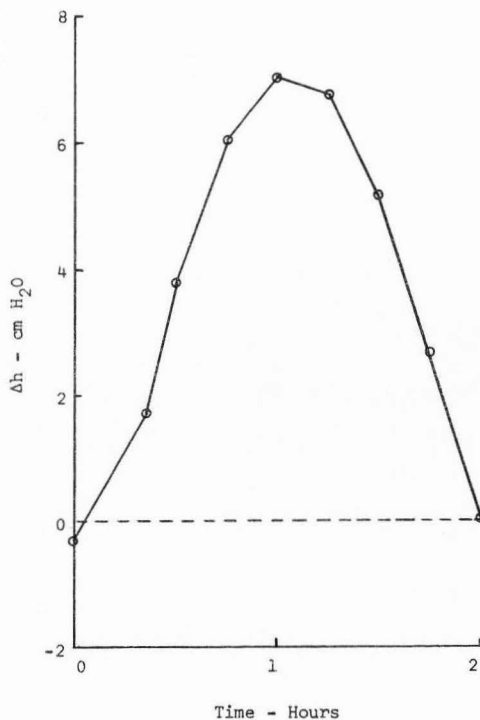


Figure 20. Pressure difference vs. time for a section of potato tuber which was subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  are for highest pressures on the cold side.

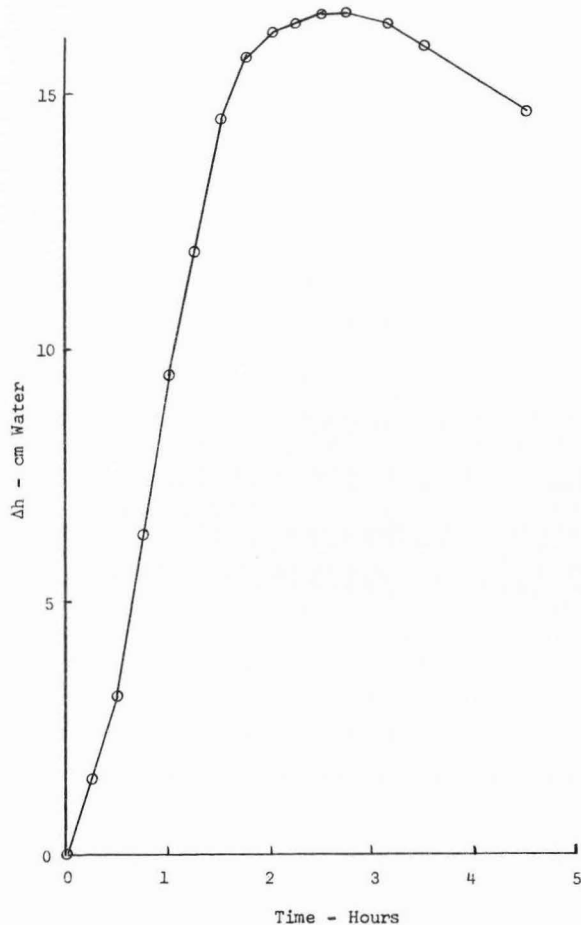


Figure 21. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate pressure buildup is on cold side.

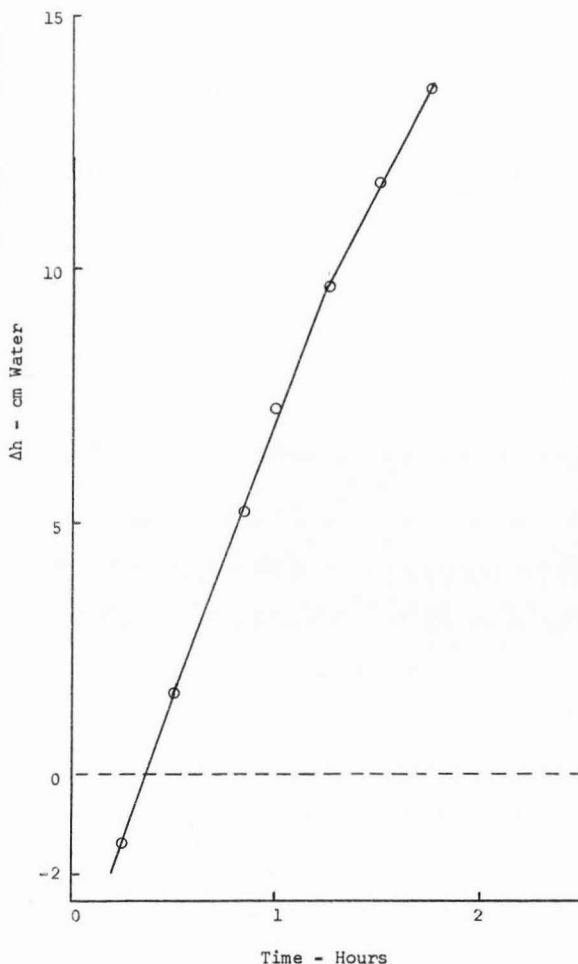


Figure 22. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate pressure is highest on cold side. After 1 hour, 45 minutes, no more readings were possible because the water had reached the top of the cold side manometer tube.

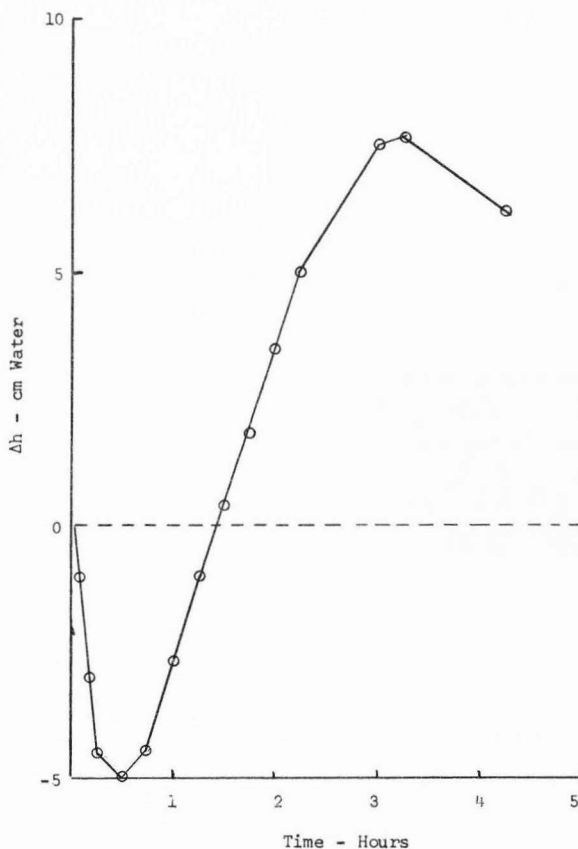


Figure 23. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a pressure buildup on the cold side. The initial dip was probably due to thermal expansion and contraction of the water and tissue.

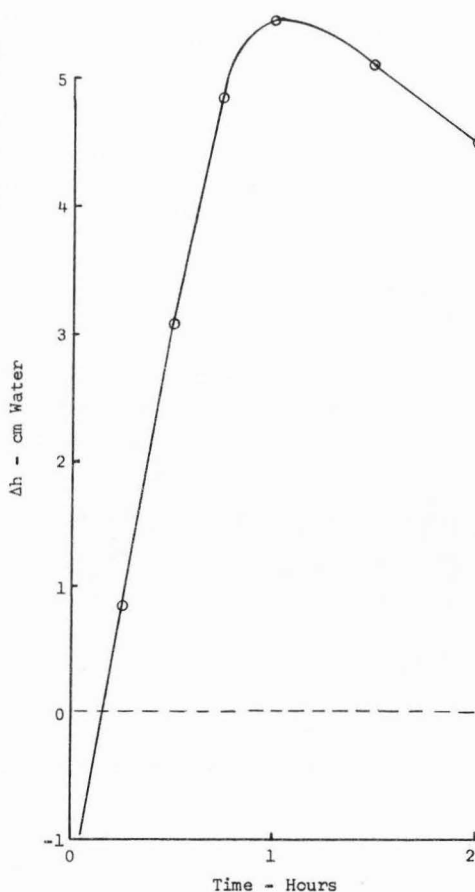


Figure 24. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a pressure buildup on the cold side.

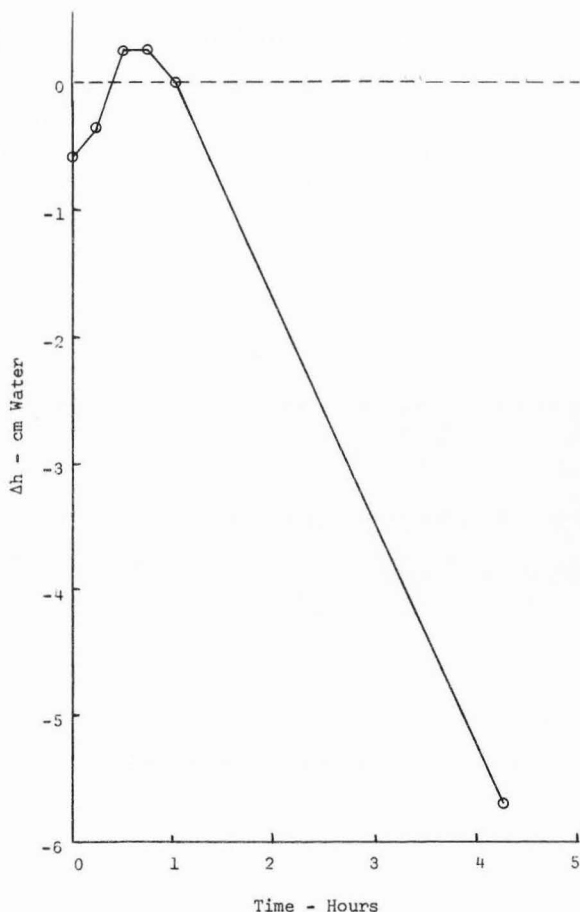


Figure 25. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a pressure buildup on the cold side. The small pressure buildup on the cold side followed by flow toward the hot side apparently indicated a more rapid movement of osmotically active materials into the water of the hot reservoir than occurred on other replications.

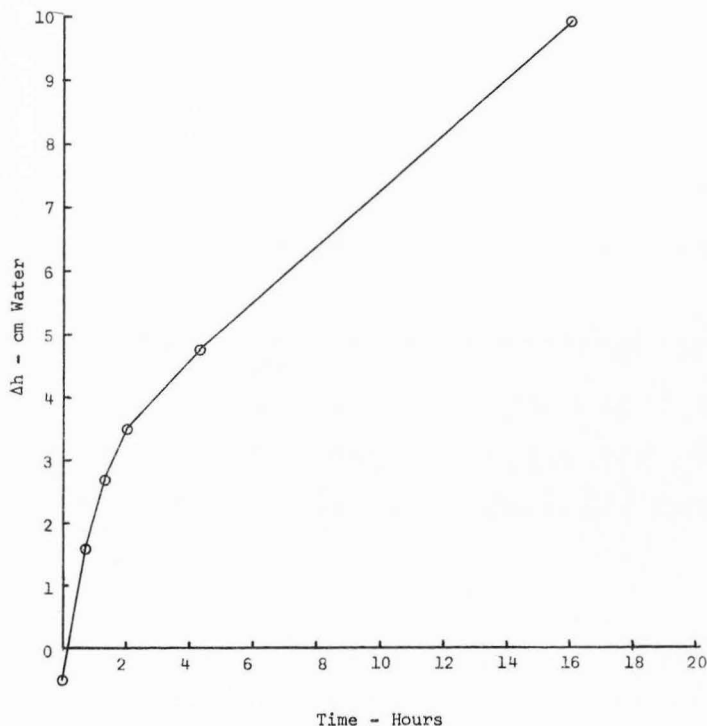


Figure 26. Pressure difference vs. time for a section of potato tuber subjected to a 6.25 centigrade degree/cm temperature gradient. Positive values of  $\Delta h$  indicate a buildup of pressure on the cold side. The sample used for this replication was placed in the apparatus for about three hours and then taken out and washed and replaced in the apparatus. This apparently prevented the buildup of osmotically active substances in the hot reservoir. The tissue is, however, much less permeable to water than were samples in other replications, probably due to the lack of aeration.



water level in the hot side manometer went up and the water level in the cold side manometer went down. This was due to the thermal expansion or contraction of the water in the reservoirs and the tissue. Flow then occurred from the hot reservoir to the cold reservoir as indicated by a drop in the hot water level and a rise in the cold water level. After about two hours, in most samples, the direction of flow reversed and water flowed from cold to hot. The average water level generally decreased as a function of time because the sample absorbed some water. It would probably be possible to correct for this using the method described by Dainty and Ginzburg (1964), but this was not done.

There was variation in the results from sample to sample, as can be seen by the figures; however, the general response was similar, indicating that thermo-osmosis actually occurs in potato tissue and that the flow is from hot to cold.

The curve shown in Figure 17 is somewhat difficult to explain, but it did not recur in other experiments. If the graph is a true picture of water movement through potato tissue and not the result of a malfunction in the apparatus, then it might be a phenomenon similar to that observed by Teorell (1962) for electro-osmosis. Oscillations of this type occur when the conditions for the linear approximation

$$J_k = \sum_{i=0}^n L_{ik} X_i$$

no longer hold. The data presented seem to indicate that the linear approximation is valid for this system if all fluxes and forces are taken into account.

All of the runs except the one represented by Figure 26 showed a buildup of pressure on the cold side followed by a reversal of the flow

and a buildup of pressure on the hot side. An investigation was made to determine the cause of this reversal. The most probable cause seemed to be a faster buildup of osmotically active substances in the hot reservoir than in the cold. To test this, samples of the water in each reservoir were collected for the replications shown in Figures 19, 20, and 21. Freezing point depression readings were made on the samples collected using the apparatus and method described in the appendix. The osmotic potentials for the samples taken are shown in Table 2. The "hours in" column is the number of hours each sample was

Table 2. Osmotic potentials and buildup rates for solutions taken from reservoirs of thermo-osmotic pressure apparatus.

Figure	Hours In	Total O.P. for Hot Reservoir joules/kg	Total O.P. for Cold Reservoir joules/kg	Rate of Buildup for Hot Reservoir joules/kg/hr	Rate of Buildup for Cold Reservoir joules/kg/hr
19	22	-296	-144	-13.45	-6.55
20	5	- 25	- 15.5	- 5.00	-3.10
21	4.5	- 62	- 40	-13.78	-8.89

in the gradient bath before the freezing point depression samples were taken. The buildup rates are calculated assuming a linear decrease of osmotic potential in the chambers. To test the assumption that the osmotic potential decreased linearly, a piece of potato tuber tissue was placed in a thermocouple psychrometer chamber similar to those described by Richards and Ogata (1958). The sample was covered with water and the psychrometer placed in the constant temperature bath. Readings

were taken over a period of twenty-four hours. The data are shown in Figure 27. This figure indicates that the assumption of a linear decrease is fairly reasonable, at least for the first ten to fifteen hours.

Some of the water collected from the reservoirs was also analyzed to determine the nature of the solutes present. Tests for starch with potassium iodide gave negative results, while the Benedict's solution test for reducing sugars gave a very positive test. Some of the solution was also titrated with sodium carbonate to determine whether organic acids were present. A graph showing milliliters of sodium carbonate added versus pH of the solution is shown in Figure 28. Two possible inflection points are shown by arrows, indicating that small amounts of organic acids may have been present.

Rather than taking the difference between the temperatures of the gradient baths as the  $\Delta T$  for solving the equations, the actual temperature difference across one of the potato tuber samples was measured using a thermocouple which could be inserted in the filling holes in the reservoirs and placed in contact with the sample. The temperatures so measured were 16 C and 23.5 C. Since the gradient baths were always controlled at the same temperatures, 16 C and 23.5 C were used to compute  $\Delta T$  for all replications.

To obtain  $Q^*$  from the data shown in Figures 17 through 26, two methods were used. The first was to take the maximum pressure difference attained and solve for  $Q^*$  using equation [10]. The other method was to determine the fluxes and forces at two different times and solve for the  $L$ 's using equation [9].

Since the data were not sufficiently smooth to apply the second

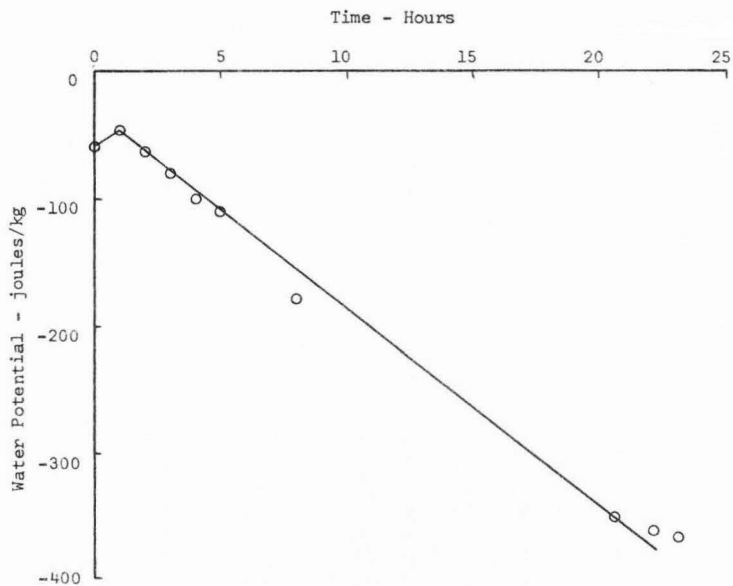


Figure 27. Graph showing the decrease of osmotic potential of water which covers a sample of potato tuber tissue.

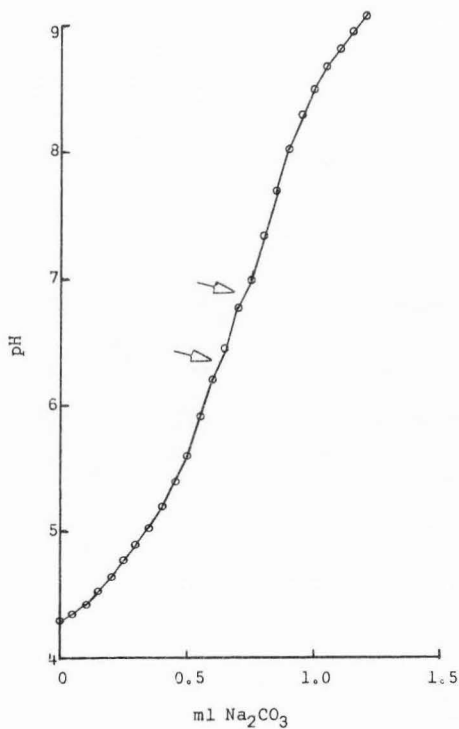


Figure 28. Graph showing a titration of the solution from one of the reservoirs of the thermo-osmotic pressure difference apparatus. The solution was diluted to 1 part in 10 and titrated with  $\text{Na}_2\text{CO}_3$ . Two possible inflection points are shown by arrows.

method satisfactorily, a quadratic equation was fitted to each of the curves using the least squares method. For an equation of the form

$$\Delta h = At^2 + Bt + C \quad [19]$$

where  $\Delta h$  is the pressure difference across the sample in cm of water and  $t$  is time, the coefficients  $A$ ,  $B$ , and  $C$  are given in Table 3 for the replications where sufficient data were available to determine the coefficients. The equations were only fitted to the points up to the

Table 3. Coefficients for the quadratic equation of best fit for the data in the figure indicated and the time indicated. The equation is of the form  $\Delta h = At^2 + Bt + C$ .

Figure	Hours Fitted	A	B	C
19	2	-3.110	12.131	- 4.913
20	1	-8.915	19.802	- 3.823
21	1.75	-3.207	17.473	- 4.792
22	1.75	-2.287	14.710	- 5.227
23	4	-1.905	16.209	-26.607
24	1	-6.688	14.663	- 2.849
26	16	-0.0261	0.948	1.373

maximum since this was the area where the best fit was desired and points beyond this would cause a poorer fit. These equations give the pressure difference,  $\Delta h$ , in cm of water at any time  $t$ . The flux of water through the potato tuber sample in  $\text{cm}^3/\text{cm}^2/\text{hr}$  at any time,  $t$ , is given by

$$5.55 \times 10^{-4} \, d(\Delta h)/dt$$

The constant,  $5.55 \times 10^{-4}$ , is calculated by taking one-half the ratio of the area of the manometer tubes to the area of the potato tuber through which flow occurs; i.e., the 3 cm diameter portion of the potato sample

inside the "O"-ring groove. The values for T and  $\Delta T$  of 293 K and 7.5 Kelvin degrees, respectively, are common to all replications, so the values for equation [9] can be calculated using the following expressions. The proper units are given for each expression.

$$\Delta P = 983.3 \Delta h \text{ ergs/gram}$$

$$v_w = .99823 \text{ grams/cm}^3$$

$$\frac{\Delta T}{T^2} = 8.7 \times 10^{-5} \text{ 1/}^\circ\text{K}$$

A computer program was written to perform these operations and calculate the L's and Q\* values. These are shown in Table 4 for several values of t. The Q\*'s are converted to joules/kg so that a comparison can be made with Q\* values obtained by other investigators and values obtained from other experiments in this study. The Q\* values shown as "max." for each run are those calculated from equation [10]. The  $\Delta P$  used was the highest value attained for all runs except those shown in Figures 22 and 26. For these, the maxima were calculated from the equations for the curves.

The values of Q\*,  $L_{ww}$ , and  $L_{wq}$  should not, in general, be functions of time. Since they appear to be functions of time from the data in Table 3, it seemed reasonable to look for a time-dependent driving force which would make these values constant as they should be. The osmotic pressure buildup shown in Table 2 seemed to furnish at least part of the necessary correction. Table 5 shows the values of  $L_{ww}$ ,  $L_{wq}$ , and Q\* where the osmotic pressure difference was added to the hydrostatic pressure difference for the three runs where osmotic pressure data were available. The values here are still time dependent, but the time dependence is reduced considerably.

Table 4. Values of  $L_{ww}$ ,  $L_{wq}$ , and  $Q^*$  calculated at 15 minute intervals using equation [9] and the data obtained from the thermo-osmotic flow experiment. The values labeled "max" were calculated from equation [10].

Figure	Time Hours	$L_{ww} \times 10^4$	$L_{wq}$	$Q^*$
		$\frac{^{\circ}\text{K cm}^4}{\text{erg. hr.}}$	$\frac{\text{cm } ^{\circ}\text{K}}{\text{hr.}}$	joules/kg
19	.50	1.25	59.4	- 47.54
	.75	1.54	62.1	- 40.34
	1.00	2.00	69.5	- 34.68
	1.25	2.87	87.6	- 30.47
	1.50	5.08	141.1	- 27.76
	1.75	2.19	582.6	- 26.56
	max.			- 38.89
20	.25	2.25	102.84	- 45.73
	.50	3.41	120.03	- 35.22
	.75	7.02	203.87	- 29.04
	1.00	11.48	311.45	- 27.14
	max.			- 27.12
21	.50	.79	100.56	-127.65
	.75	.89	103.23	-115.43
	1.00	1.03	108.34	-104.78
	1.25	1.23	117.24	- 95.67
	1.50	1.50	132.51	- 88.09
	1.75	1.95	159.78	- 82.05
	max.			- 63.54
22	.50	.64	83.08	-130.17
	.75	.71	84.27	-119.28
	1.00	.79	86.61	-109.52
	1.25	.90	90.59	-100.85
	1.50	1.04	96.95	- 93.28
	1.75	1.23	107.05	- 86.79
	max.			- 70.64
23	2.5	1.10	51.19	- 46.59
	3.0	1.65	61.47	- 37.37
	3.5	3.27	104.11	- 34.15
	max.			- 29.57
24	.25	2.29	75.73	- 33.03
	.50	3.51	88.92	- 25.34
	.75	7.48	156.01	- 20.87
	1.00	57.49	1128.49	- 19.63
	max.			- 19.56



Table 4 continued.

Figure	Time Hours	$L_{ww} \times 10^4$	$L_{wq}$	$Q^*$ joules/kg
		$\frac{^{\circ}\text{K cm}^4}{\text{erg. hr.}}$	$\frac{\text{cm } ^{\circ}\text{K}}{\text{hr.}}$	
26	0	.094	6.55	-69.90
	4	.113	6.78	-60.14
	8	.155	7.75	-49.93
	12	.248	10.67	-42.94
	16	.623	24.40	-41.71
	max.			-38.34

Table 5. Values of  $L_{ww}$ ,  $L_{wq}$ , and  $Q^*$  calculated using equation [9] and using the difference in hydraulic pressure plus the difference in osmotic pressure between the reservoirs as a driving force.

Figure	Time Hours	$L_{ww} \times 10^5$	$L_{wq}$	$Q^*$ joules/kg
		$\frac{^{\circ}\text{K cm}^4}{\text{erg. hr.}}$	$\frac{\text{cm } ^{\circ}\text{K}}{\text{hr.}}$	
19	.50	1.38	66.57	-482.94
	.75	1.41	66.98	-475.77
	1.00	1.44	67.61	-470.31
	1.25	1.47	68.50	-465.87
	1.50	1.50	69.65	-463.14
	1.75	1.54	71.08	-462.12
20	.25	9.09	116.83	-128.53
	.50	10.54	124.38	-118.02
	.75	12.54	140.17	-111.81
	1.00	15.47	170.00	-109.90
21	.50	1.69	109.13	-645.73
	.75	1.73	109.87	-633.79
	1.00	1.78	110.93	-622.87
	1.25	1.83	112.33	-613.99
	1.50	1.88	114.10	-606.14
	1.75	1.94	116.27	-600.34

Other experiments on thermo-osmotic  
pressure difference

Several experiments were conducted using the thermo-osmotic apparatus described in the previous section to determine whether flow occurred through other membranes besides living potatoes.

The first experiment was conducted using the potato sample that was used to collect data for Figure 26. The water was emptied from the reservoirs and the sample was frozen by cooling it to  $-40^{\circ}\text{C}$  for one hour. The sample was then washed and the apparatus reassembled and placed in the gradient bath. Readings were taken for two hours, and the manometers were checked periodically for about five more hours. No measurable flow took place.

The next experiment was conducted with a 2% agar membrane. The membrane construction was similar to that described by Ackers and Steere (1962). A ring was machined from brass to clamp a double thickness of about 60 mesh nylon cloth in the chamber of the apparatus. The agar sol was poured onto the cloth and allowed to gel. This gave a well-supported membrane about 0.3 cm thick.

The agar seemed to absorb water initially, and the cold water was apparently absorbed more rapidly than the hot, giving the appearance of flow through the membrane. The pressures stayed the same, however, when the temperature gradient was reversed. If a membrane previously soaked in water was used, no change in the manometers was observed.

An experiment similar to the one just described was conducted using a 1.2 cm thick, 10% gelatine membrane. The results were similar to those obtained when agar was used.

With both the agar and gelatine membranes, one reservoir was filled with a one molar manitol solution while pure water was left in the other

reservoir. An initial pressure buildup was observed on the manitol side, which decreased again over a period of several days.

Slices of carrot root were also tried in the apparatus to determine whether thermo-osmosis would occur. The carrot root samples were prepared in a manner similar to that used to prepare potato tuber samples as described earlier. The entire cross section was used, including xylem, phloem, and storage tissue. Although the results obtained from the carrot experiments were at times erratic, no data were obtained which indicated thermally induced water flow. The conclusion reached was that thermo-osmosis was negligible in carrot tissue.

## DISCUSSION AND CONCLUSIONS

General

Several observations may be made about the results of all the experiments conducted.

1. Thermo-osmosis occurred in both saturated and unsaturated potato tuber tissue. All experiments indicated that water had moved as a result of a thermal gradient.

2. The direction of flow in potato tubers was, with very few exceptions, toward the cold side of the tissue. The few cases where flow occurred from cold to hot could be accounted for by osmotic pressure differences, and were, therefore, not flows caused by a thermo-osmotic driving force.

3. Water potential gradients ranging from 0.4 joules/kg/C° to 2.36 joules/kg/C° for the saturated case and from 7.0 joules/kg/C° to 24.3 joules/kg/C° for the unsaturated were built up due to temperature gradients in the potato tuber sample. Water potential gradients of this magnitude may be of considerable importance in permeability and flow studies where temperature gradients exist.

4. No thermo-osmosis was observed in saturated carrot tissue, saturated 2% agar, saturated gelatine, or frozen potato tuber tissue.

5. The time or space dependence of  $Q^*$  in all experiments indicated that other fluxes and forces are present which are not accounted for in the two-component treatment presented here.

### Thermo-osmotic membranes

The fact that thermo-osmosis occurs in live potato tuber tissue and not in frozen potato, saturated carrot, agar, or gelatine would seem to substantiate the theory on membrane construction presented earlier. Water flow in potato tuber tissue probably takes place through cell membranes which represent relatively high energy barriers. Such membranes would probably be quite selective in passing either high or low energy molecules depending on the nature of the membrane.

On the other hand, water flow through a cross-section of carrot root would probably take place primarily through the xylem. The activation energy for water flow through xylem tissue is lower than for water flow through cell membranes (see Jensen, 1961), and the pores through which water passes are much larger. One would, therefore, expect a thermo-osmotic effect in carrot xylem to be small, possibly too small to be separated from effects due to experimental error.

The results of the experiments with agar and gelatine membranes can be interpreted in much the same way. The pores in these membranes are apparently relatively large, as was shown by the diffusion of mannitol through them. Such large pores would not be expected to give rise to measurable thermo-osmosis. The same reasoning may be applied to the frozen potato tissue. The membranes through which flow occurs are destroyed by freezing; thus, the system would probably be similar to the gelatine or agar membrane, and no thermo-osmosis would be expected.

The degree to which irreversible thermodynamics and kinetic theory are able to explain, at least qualitatively, these experimental results indicates the value of using these disciplines to analyze some biological systems.

It should be pointed out that although saturated carrot root xylem showed no thermo-osmosis, unsaturated xylem might show a considerable thermo-osmotic effect. As some of the larger pores empty, water flow may occur in the vapor phase or as tightly adsorbed films. In either case, the activation energies would increase and thermo-osmosis would be expected to occur.

Properties of cell membranes as indicated  
by thermo-osmosis experiments

As was pointed out earlier, the direction of flow of a liquid through a membrane which is subjected to a thermal gradient may give some insight into the nature of the membrane. Membranes which present a positive energy barrier (Figure 5) to the flow of the substance favor the passage of higher energy molecules, while energy "ditches" (Figure 7) favor the passage of lower energy molecules. Two membrane models were presented in the literature review, each suggesting a different mode of transfer of water through the membrane. In the first model, water would have to pass through the hydrophobic lipid layer forming a pore as it went. This type of membrane presents an energy barrier to the crossing water molecules and only molecules with energies equal to or higher than the activation energy of the membrane can cross. The second membrane model contained protein pores which extended through the lipid layer. Water movement was supposed to take place through these hydrophilic pores. The pores present an energy "ditch" which facilitates the crossing of a relatively larger number of low energy molecules (see Spanner, 1954).

Assuming that either one or the other of these models is correct, and that water movement takes place through the cell membranes, the data

collected in this experiment should indicate which path is taken by water molecules. The direction of water flow observed, from hot to cold, indicates that the water passes through the lipid layer. There could be several explanations for this. If protein pores exist, then more water might be passing through the lipid layer than through the protein. If no protein pores exist, then the second membrane model is incorrect. Another possibility is that the water may not move through the cells at all, but through the intercellular spaces. In any case, the information is interesting and suggests further research on this subject.

#### Size of $Q^*$ values

Since to the author's knowledge no work on thermo-osmosis in living membranes has been published, the  $Q^*$  values obtained can only be compared to the values for cellophane membranes by Haase and Steinert (1959) and the values for soil given by Taylor (1963). The results of the theoretical work by Spanner (1954) should also be compared to the values obtained here.

The values of the apparent heat of transfer shown in Table 1 can be compared to the values calculated from Taylor and Cavazza (1954), and presented by Taylor (1963). The two systems are quite different and one would not expect good agreement, but such a comparison is made because both systems give values of  $Q^{a*}$ , and no data on  $Q^{a*}$  are available for any other unsaturated liquid-membrane system. The range of  $Q^{a*}$  for potato tissue taken from Table 1 is from 1908.2 joules/kg to 6741.6 joules/kg. The approximate value from Taylor (1963) at a similar water potential is  $2 \times 10^5$  joules/kg. The difference is not surprising since the water in the unsaturated soil moves as vapor, and the liquid to

vapor transition has a much higher activation energy than does the flow through cell membranes.

The values of  $Q^*$  for potato tissue which would seem to be most correct are those in Table 5, since the total water potential gradient has been taken into account. The averages of each of the three runs presented are 472 joules/kg, 118 joules/kg, and 622 joules/kg. Data from Haase and Steinert (1959) give values of  $Q^*$  for various weight cellophane membranes. Representative values are 523 joules/kg for 300 g/m<sup>2</sup> cellophane at 21 C, and 6360 joules/kg for 600 g/m<sup>2</sup> cellophane containing  $\text{Ca}_2\text{Fe}(\text{CN})_6$  at 22.5 C. Taylor and Cary (1960) found values of about 3 joules/kg for saturated Millville silt loam soil. It is seen from this that the values of Haase and Steinert (1959) agree very favorably with those obtained for potato tuber tissue. The fact that values for saturated soil are considerably smaller is not surprising since pores are probably larger and activation energies lower for saturated water flow. The variability of  $Q^*$  from sample to sample seems to be quite large, but large variations were also observed by Haase and Steinert (1959) for cellophane membranes. No explanation of this is immediately evident, and more research is necessary before this type of variation can be explained.

Using the Spanner equation (see Spanner, 1954) and a  $Q_{10}$  of 2.3, a 1 centigrade degree temperature gradient would be equal to a driving force of about 13,200 joules/kg. Experimental results gave driving forces of about 2 joules/kg/C° for saturated samples and 25 joules/kg/C° for unsaturated samples. Neither of these values approaches that of Spanner. This indicates either that some of the assumptions for Spanner's derivation need to be examined, or that the experimental results presented



here are wrong. The agreement of the  $Q^*$ 's found in this study with those obtained by Haase and Steinert (1959) and Taylor and Cary (1960) give some confidence that the latter is not true.

#### Time and space dependence of $Q^*$

The time dependence of  $Q^*$  as shown in Tables 3 and 4 and the space dependence (possibly water potential or water content dependence) of the  $Q^{a*}$ 's in Figure 1 indicate that the system has not been completely described by the two-component model presented here. A look at the nature of the sample will reveal some possible corrections or additions. Two possibilities are apparent. First, because the cell is a dynamic system, chemical reactions are constantly taking place. Various chemical species are continually changed into others which may be more or less osmotically active than the original species. Since such reactions would take place more rapidly at the hot end of the sample than at the cold end, an osmotic pressure gradient would be built up in the tissue. The second possibility is that linked transfer between solutes and heat or water or both occurs. This also seems reasonable because linked transfer may occur between any or all of the components.

If we assume that these processes are occurring, the proper analysis would involve solving the following equations:

$$\begin{aligned}
 J_w &= L_{ww}X_w + L_{wq}X_q + L_{wr}X_r + L_{ws}X_s \\
 J_q &= L_{qw}X_w + L_{qq}X_q + L_{qr}X_r + L_{qs}X_s \\
 J_r &= L_{rw}X_w + L_{rq}X_q + L_{rr}X_r + L_{rs}X_s \\
 J_s &= L_{sw}X_w + L_{sq}X_q + L_{sr}X_r + L_{ss}X_s
 \end{aligned}
 \tag{20}$$

where r and s indicate chemical reactions and solutes respectively.

Evaluating the necessary fluxes and forces for such an analysis would

be an almost impossible task using techniques now available. It seems, therefore, that although heat and water flow in plant tissue cannot be completely described by a two-component model, it furnishes a good first approximation.

## SUGGESTIONS FOR FUTURE WORK

In deciding where future emphasis should be placed, the importance of or interest in a piece of information should not be the only consideration. Some thought should be given to the feasibility of the study in the light of present research methods and techniques. Thus, the solution of equations [20] would seem to be a good subject for future work. However, when one considers the possible knowledge gained for the time required, at least for present research techniques, this does not appear to be a fruitful area in which to work.

There are, however, several areas of study suggested by this work which may be fruitful.

The relationship between positive and negative energy barriers and the sign of  $Q^*$  should furnish an important tool for research in membrane structure. Also, the magnitude of  $Q^*$  may be indicative of membrane properties. It is felt that a study of the thermo-osmotic properties of artificial membranes having known chemical composition and physical properties would yield the information necessary for analyzing the structure of naturally occurring membranes. Such membranes might be deposited on or in membranes which have been found to be inactive in a thermo-osmotic sense such as agar or sintered-glass.

Another field of study is the determination of the relationship between the activation energy of a membrane and its  $Q^*$  value. Cary (1965) states that the heat of transfer for a system is some fraction of the activation energy, this fraction being one (1) for evaporation. More

work needs to be done on the kinetics of water transfer due to heat flow to determine what this fraction is for various systems. If some valid kinetic model can be constructed and a reliable method for determining the fraction can be found, then the calculation of  $Q^*$  from  $Q_{10}$  values as was suggested by Spanner (1954) may be useful.

A third area in which fruitful research might be done is the study of the movement of sugars, hormones, and other materials with heat. Such a study might give some insight into photo-tropisms and inter-cellular transport processes.

There are two levels at which thermo-osmotic phenomena may be important, the tissue level and the intercellular level. The study presented here deals with thermo-osmosis on a tissue level and shows it to be an important phenomenon in some tissues. The importance of thermo-osmosis may be even greater at the cellular level. The methods of Dainty and Ginzburg (1964) may be adaptable to some thermo-osmosis studies using single large cells such as Nitella, but new techniques will be required for intercellular studies.

The measurement of intercellular temperature gradients would be a step in assessing the importance of thermo-osmosis at an intercellular level. Such measurements might be possible using infra-red photography or specially-constructed infrared microscopes.

From the few suggestions presented here, it is easily seen that much remains to be done before even an elementary understanding of the role of thermo-osmosis in plants is obtained. It is felt, however, that the study presented here furnished valuable information which may be of considerable use in future studies.

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## APPENDIX



THE CONSTRUCTION AND USE OF A FREEZING POINT  
DEPRESSION APPARATUS

The apparatus constructed to measure the freezing point depression of samples of solution was similar in some respects to that described by Marr and Vaadia (1961), although many modifications were made.

The sample holder and thermistor probe are shown in Figure 29. The circuit is shown in Figure 30. The sample holder and probe were constructed from 1/2 inch brass stock. The sample chamber was drilled out with a number 4, 60° countersink bit. The large part of the hole was 5/16 inch diameter, and the small part was 1/8 inch. The thermistor holder was machined to fit tightly into the large part of the sample holder. The thermistor hole was drilled so that the thermistor, when in place, fit in the center of the small hole. The plastic tube was for ease in handling the apparatus. A wheatstone bridge and potentiometer recorder<sup>1</sup> were used to measure the resistance of the thermistor and thus the temperature of the sample.

Readings were taken by filling the sample chamber with a known amount of solution and placing the apparatus in a test tube which was in a Dewar flask filled with dry ice. The sample super-cooled and then froze, releasing its latent heat of fusion. This brought the temperature back up to the freezing point for a very short time. The lag of the thermistor and recorder seemed small enough so that this point defined the osmotic potential. Since the apparatus was calibrated using water and potassium chloride solutions of known osmotic pressure, the

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<sup>1</sup>Leeds and Northrup Company, Philadelphia, Pennsylvania.

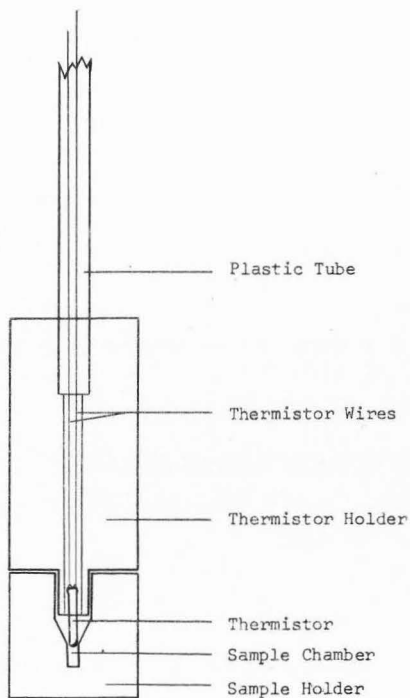


Figure 29. Probe and sample holder for measuring freezing point depression.

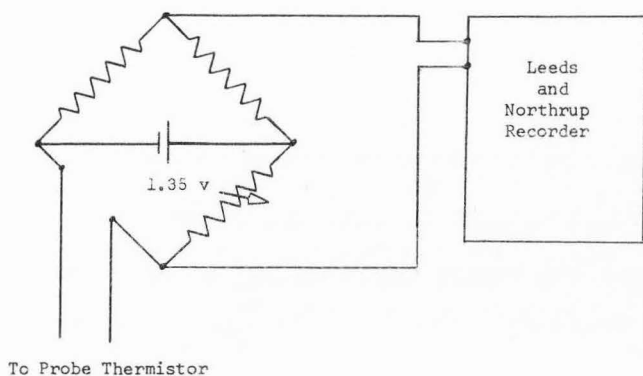


Figure 30. Circuit used to measure freezing point depression.

method did not depend on measuring the actual freezing point temperature, but on a comparison with a known sample. The readings taken using this method were repeatable to 8 joules/kg or better in the range from zero to 400 joules/kg.

The only precautions which seemed necessary are: (1) The same amount of sample should be used for each determination. (2) Freezing should not be too fast. A test tube in dry ice seems to give about the right amount of cooling. (3) Use a fast enough recorder chart speed so that the minimum point obtained when the sample freezes can be readily detected.